

GAW Report No. 227

# WMO/GAW Aerosol Measurement Procedures, Guidelines and Recommendations

2<sup>nd</sup> Edition

2016

WEATHER CLIMATE WATER



WORLD  
METEOROLOGICAL  
ORGANIZATION

WMO-No. 1177



GLOBAL  
ATMOSPHERE  
WATCH



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### EDITORIAL NOTE

METEOTERM, the WMO terminology database, may be consulted at:

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## PREFACE

The World Meteorological Organization (WMO) Executive Council, through actions initiated by the Commission for Atmospheric Science (CAS) and its Environmental Pollution and Atmospheric Chemistry Scientific Steering Committee (EPAC SSC), has placed high priority on improving the quality and spatial coverage of Global Atmosphere Watch (GAW) measurements. The WMO Scientific Advisory Group on Aerosol (SAG Aerosol) was established in 1997 to implement the aerosol measurement programme in GAW that addresses not only climate-related, but also air quality issues. For developing countries in particular, regional aerosol pollution issues are frequently of concern. The SAG Aerosol recognizes that measurements directed at climate and regional environmental problems can frequently involve common methods.

A key role of the SAG Aerosol is drafting guidelines for measurements, proposing standards for compatible observations, quality assurance and common systems for calibration, data analysis and data archiving. This document is second edition of the guidelines, updating the first edition that was published in 2003.

WMO has a history of organizing aerosol measurements, as reflected in its promotion of monitoring stations globally, and workshops particularly focused on aerosol optical depth (AOD) such as those in 1986 (WMO/GAW Report No. 43) and 1994 (WMO/GAW Report No. 101). This report expands the guidelines on aerosol measurements from AOD to include a comprehensive list of aerosol optical, physical and chemical measurements that are needed globally. It provides assistance to those involved in developing an integrated global aerosol measurement system for climate and atmospheric composition studies. It should be considered a living document that will be updated and revised according to new scientific and technological developments. Recognizing that a printed report may not be able to keep up with advances in measurement technology, users of this report are advised to check the SAG Aerosol website for updates to this report. The most recent update to this report can be found at <http://www.wmo-gaw-wcc-aerosol-physics.org/wmo-gaw-reports.html>.

The mention of specific manufacturers and instrument models does not imply an endorsement either by WMO or by the authors of this report.

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## CHAPTER 1. INTRODUCTION

It is the goal of the Global Atmosphere Watch (GAW) programme to ensure long-term measurements in order to detect trends in global distributions of chemical constituents in air and the reasons for them (WMO, 2001a). With respect to aerosols, the objective of GAW is to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality on multi-decadal time scales and on regional, hemispheric and global spatial scales. The objective of GAW Report No. 153, published in 2003, was to provide a synthesis of methodologies and procedures for measuring the recommended aerosol variables within the GAW network. The report has been extensively used by the scientific community, and more particularly by scientists and engineers involved with data production from ground-based sites. The knowledge of aerosol impact on climate and air quality as well as the techniques used for the determination of the essential aerosol variables to be monitored at ground-based sites have considerably evolved in the last decade, justifying an update of GAW Report No. 153.

This update has been prepared shortly after the release of the Working Group 1 report from the International Panel on Climate Change (IPCC, 2013). A clear emphasis was given for the first time in IPCC reports since 1992 to the analyses of evidence of climate change from observations of the atmosphere highlighting the challenges for developing long-term, high quality observation record that can be used to constrain models at global and regional scales. While the benefit of improved monitoring capabilities developed in the last decades, both from satellites and ground-based has been clearly assessed for the production of more reliable data records, the report still highlights the need for maintaining and enhancing the capacity of the observing system to provide the additional constrains, in particular for the derivation of trends.

This is particularly true for aerosol and clouds which continue to contribute to the largest uncertainty in estimates and interpretations of the Earth's climate. In substance, the magnitude of aerosol forcing is assessed to be  $-0.45$  ( $-0.95$  to  $+0.05$ )  $\text{W m}^{-2}$  for aerosol alone and  $-0.9$  ( $-1.9$  to  $-0.1$ )  $\text{W m}^{-2}$  when aerosol/cloud feedbacks are accounted for, both with medium confidence level. The uncertainty is still very high although substantial progress has been made to understand climate-relevant aerosol processes, such as new particle and secondary organic aerosol formation mechanisms, or aerosol source attribution. The substantial impact of anthropogenic emissions is also better quantified both in terms of contribution to change in optical depth or in cloud condensation nuclei concentration.

A consistent picture is now the observation of important regional variability for the aerosol burden showing an apparent decline over Europe and the eastern USA since the mid 1990s and, on the contrary, an apparent increase over eastern and southern Asia in the last decade (Asmi et al., 2013; Collaud Coen et al., 2013). These new results are direct products of the structuration efforts initiated more than 10 years ago to better coordinate the data production system and its diffusion to the entire scientific community in particular in Europe and in North America. Elsewhere in the world, the lack of in situ time series does not allow to derive any long-term trends to reach statistical significance. The lack of information along with the strong interannual variability, the regional heterogeneity of particle loads and the limited time span of the available records still limits the identification of long-term trends in aerosols.

The recognition that climate induced feedbacks may lead to amplification or dampening of the aerosol/cloud climate forcing is also highlighted by recent studies leading to an even more complex picture that partly explains why uncertainties in forcing estimates remains high. The physical, chemical and biological mechanisms that produce primary and secondary aerosol particles will be modified by climate change mainly through both temperature increase and change in precipitation, so there is the potential for important climate feedbacks. Quantification of climate-induced feedbacks may be as high as  $+1$   $\text{W m}^{-2}$  globally for natural processes only by the end of the century (Carslaw et al., 2010). In parallel, stronger regulations on anthropogenic emissions for improving air quality will impact on particle burdens, impacting on forcing at least at the regional scale. Climate change coupled with air quality regulations will therefore increase the number of drivers of change in a very complex

coupled system (Monks et al., 2009; Fowler et al., 2010, Isaksen et al., 2009). The accuracy with which sources, transport and sinks of aerosol can be determined and the capacity to detect long-term trends and feedbacks for prediction of climate change will be essential in the future.

A strong recommendation from the report is therefore to pursue and further develop the observation effort to quantify and understand the current perturbation of the atmosphere towards the establishment of a sustainable system of which GAW is an essential pillar. Presently, WMO's GAW network consists of 28 Global stations and numerous Regional stations that cover different types of aerosols including: clean and polluted continental, marine, arctic, dust, biomass burning, and free tropospheric particles. Data are centralized in the World Data Center for Aerosol (WDCA) hosted by the Norwegian Center for Air Research (NILU) and in open access to the entire scientific community.

GAW's Scientific Advisory Group (SAG) on Aerosols recommended the development of a global aerosol network of ground-based stations (see WMO GAW Report No. 207) and identified a list of comprehensive aerosol measurements to be conducted at some stations as well as a subset of core measurements to be made at a larger number of stations. Global stations are expected to measure as many on this list as possible while the GAW Regional stations and contributing partner network stations will measure the smaller set of core aerosol observations, to complete the global coverage.

**Table 1.1. List of aerosol measurements that are recommended by the GAW Scientific Advisory Group on Aerosols for long-term measurements in the global network**

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**Continuous Measurement**

Column and Profile:

- aerosol optical depth (various wavelengths)
- vertical profile of aerosol backscattering coefficient
- vertical profile of aerosol particle extinction coefficient

Optical Properties:

- particle light scattering coefficient (various wavelengths)
- particle light hemispheric backscattering coefficient (various wavelengths)
- particle light absorption coefficient (various wavelengths)

Physical Properties:

- particle number concentration (size-integrated)
- particle number size distribution
- particle mass concentration (two size fractions)
- cloud condensation nuclei number concentration (at various super-saturations)

Chemical Properties:

- particle mass concentration of major chemical components (two size fractions)

**Intermittent or Continuous Measurement**

- particle size-segregated chemical composition
  - Dependence of aerosol properties on relative humidity
- 

Methodologies and procedures for measuring the recommended aerosol variables are presented in the following chapters. They have been evolving since 2003 both because more advanced instrumentation is now available and because efforts from the scientific community allowed for the development of more suited operation procedures for monitoring purposes. The result is that, contrary to 2003, the GAW SAG Aerosol can now recommend Standard Operating Procedures (SOPs) for almost all recommended aerosol measurements in Table 1.1. Technical issues such as acquisition and processing of space and in situ observations (near-real-time, historic and ancillary), analysis and forecasting, product generation, dissemination, archiving, and production of decision-making support tools as well as use of

data in climate-chemistry models will be of primary importance in the future. Clearly, technologies are evolving and current research instruments may be used in the future for monitoring operations (see Laj et al. 2009). On-line aerosol chemistry measurements with aerosol mass spectrometers or single-particle refractory black carbon measurement with incandescence techniques are now implemented at some stations in monitoring configuration. An implementation plan for these measurements in GAW, however, requires SOPs and data formatting recommendations, which still do not exist for these new measurements, before diffusion of information.

Improving data quality and enhancing their use by the scientific community is an essential aim within GAW. In this context, it is recommended that station operators work jointly with World Calibration Centres (WCC) and in particular with the WCC for aerosol physics (WCCAP) hosted by the Leibniz Institute for Tropospheric Research (TROPOS) in Leipzig, Germany and with the World Optical Depth Research and Calibration Center (WORCC) hosted by the Physical and Meteorological Observatory/World Radiation Center (PMOD/WRC) in Davos Switzerland for aerosol optical depth. Establishment of additional WCC, in particular for aerosol chemistry is in the GAW roadmap to maintain Quality Assurance (QA) at GAW sites.

At the core of the GAW global network of Global, Regional and contributing partner stations is a willingness on the part of the participating organizations to pool their observations and make them publicly available. GAW participants endeavour to provide precise, accurate and timely observations of the aerosol parameters listed in Table 1.1. In order to achieve this and as important information for the user community, the data available from the WDCA should have certain characteristics:

- 1) They should be traceable to the original raw observational data. This requires the maintenance of an archive of the raw data, and the history of the processes applied to that data in deriving the processed data series submitted to WDCA. Such archives are normally the responsibility of the participating organization; however, the WDCA can provide limited assistance as an 'archive of last resort' where the alternative is the loss of the data.
- 2) They should be of known quality which often requires participation in intercalibration exercises provided by the WCC or within specific programmes.
- 3) They should include all the information required by a user to permit the sensible use of the data and comply with the proposed data formatting of the WMO Information System (WIS). This is of particular importance in an organization like GAW where different participants may use different methods to measure individual parameters. They should include a contact point for the participant submitting the data. This aids the sensible use of the data and helps users recognize the work of the participants.

A long-term goal of the GAW aerosol data analysis and synthesis activities is to work with the GAW Global and Regional stations as well as contributing partner networks and satellite monitoring agencies to produce an integrated set of global aerosol observations. This is being done under the Integrated Global Observing Strategy (IGOS) established in 1998 by a comprehensive consortium of satellite and non-satellite observational agencies and organizations. It is also described in the IGOS-IGACO Report (2004).

Finally, the most essential factor to implement the aerosol observing system is often related to education and training. Building the human capacity for both providing high quality information and ensuring effective use of data within national/international policy frameworks or to respond to new scientific challenges will require maintaining and developing the proper level of scientific and technical expertise, in particular linked to data provision, storage and diffusion, relevant to the GAW activities. This is certainly one of the most challenging tasks for the future.

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## CHAPTER 2. SAMPLING TECHNIQUES AND CONSIDERATIONS

There are many issues related to sampling techniques that need careful consideration. The sections below deal with issues related to particle size separation and inlets, sampling media and methods, sampling setups, flow measurement and sampling frequencies. An ideal aerosol sampling system:

- Excludes precipitation from the sampled aerosol
- Provides a representative ambient aerosol sample with minimal diffusional and inertial losses
- Provides aerosol particles at a low relative humidity (< 40%)
- Minimizes the evaporation of volatile particulate species.

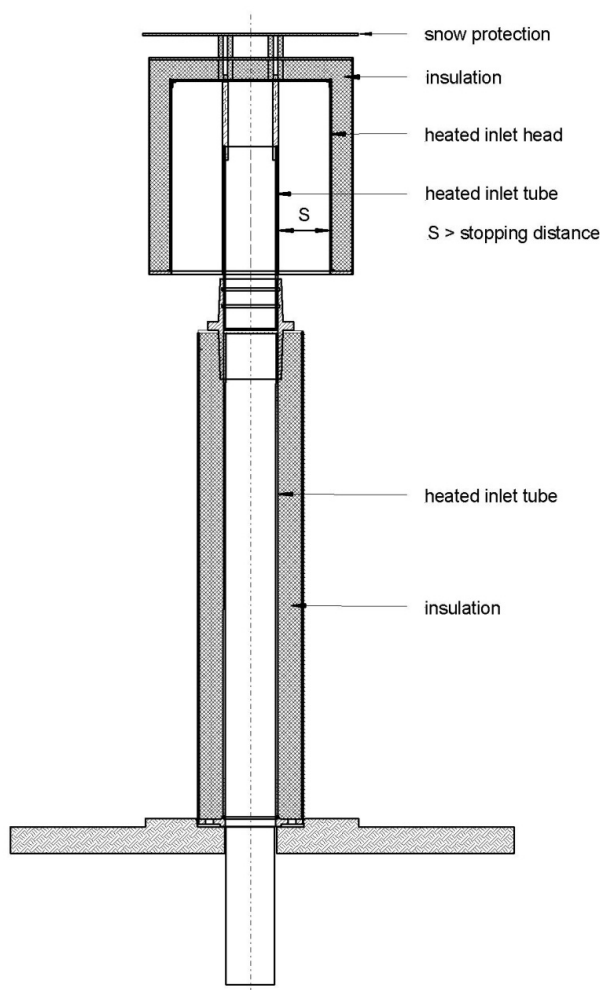
In this section, we provide guidelines for the common sampling considerations that apply to most aerosol analysers and samplers at Global and Regional GAW stations. The inlet used for aerosol sampling should meet certain design guidelines so that an undisturbed aerosol is delivered to sampling or measurement instrumentation. The purpose of the inlet system is to provide a sample aerosol that is representative of ambient air, but at a controlled relative humidity, to the various aerosol analysers and samplers in the field laboratory. Humidity control is desirable because of the strong influence of relative humidity on the size of most airborne particles. It is also necessary to exclude precipitation, and special care in sampling is required at stations that frequently are immersed in clouds. The most common set-ups combine an outdoor aerosol inlet, smooth transport pipes, an aerosol conditioner to dry the sampling flow, and a final flow splitter to distribute the aerosol among the various instruments and samplers. Aerosol instrumentation should generally be housed in a room that provides a clean laboratory environment and temperatures between 15 and 30°C. Optimum indoor temperatures range between 20 and 25 °C.

### 2.1 Inlet design considerations

For instrumental measurements, sample air should be brought into the laboratory through a vertical stack with an inlet that is high enough above ground level to minimize local influences. For sites without surrounding obstructive vegetation, topography or buildings, a minimum height of 2 m above the roof of the laboratory is recommended. However, obstructed sites may require even higher inlets, to avoid influence by the surroundings. If possible, the sampling duct should be brought through the roof of the laboratory. If this is not possible, then a gradual bend in the inlet pipe is acceptable. Because atmospheric trace gas analysers may have requirements incompatible with aerosol inlets, an inlet stack dedicated to aerosol sampling is normally required.

An omni-directional high efficiency air inlet is required for aerosol sampling. In other words, it should have a high aerosol transmission efficiency that does not vary with wind direction or wind speed. This can be achieved with a vertical air duct with a cover that excludes drizzle, rain and snow mounted on top of the inlet duct. The inlet should have a particle cut-off diameter of 10 micrometres aerodynamic diameter under ambient conditions.

Alternative inlet designs should be considered for measurements in an extreme climate. Sampling sites that experience frequent clouds, fog or freezing may prefer using a heated whole-air inlet to capture cloud and fog droplets within the sample. This inlet is recommended for sites that are immersed in fog or cloud more than 10% of the time, which is commonly encountered on high Alpine mountains. Figure 2.1 illustrates the concept of such a heated whole-air inlet based on the design of the inlet of the Jungfrauoch station in Switzerland as described in Weingartner et al. (1999) and Wiedensohler et al. (2014). Controlled heating prevents clogging of the inlet with ice. Inside the inlet, cloud and fog droplets are evaporated, so that all aerosol particles, whether activated or not, will be included in the measurement. For such whole-air inlets it is desirable to scrutinize the relationship between the ambient wind velocity and variations in the size-cut characteristics.



**Figure 2.1. Sketch of a whole air inlet**

## 2.2 Size cut-offs

The particle cut-off size of the aerosol inlet and the height above ground are usually guided by the purpose of the measurement network. The most widely used options are currently  $PM_{10}$ ,  $PM_{2.5}$ , or  $PM_{1}$ , implying upper aerodynamic cut-off diameters at 10, 2.5, and 1  $\mu\text{m}$ , respectively, under ambient conditions. These inlets are based on particle separation by either an impactor or a cyclone.

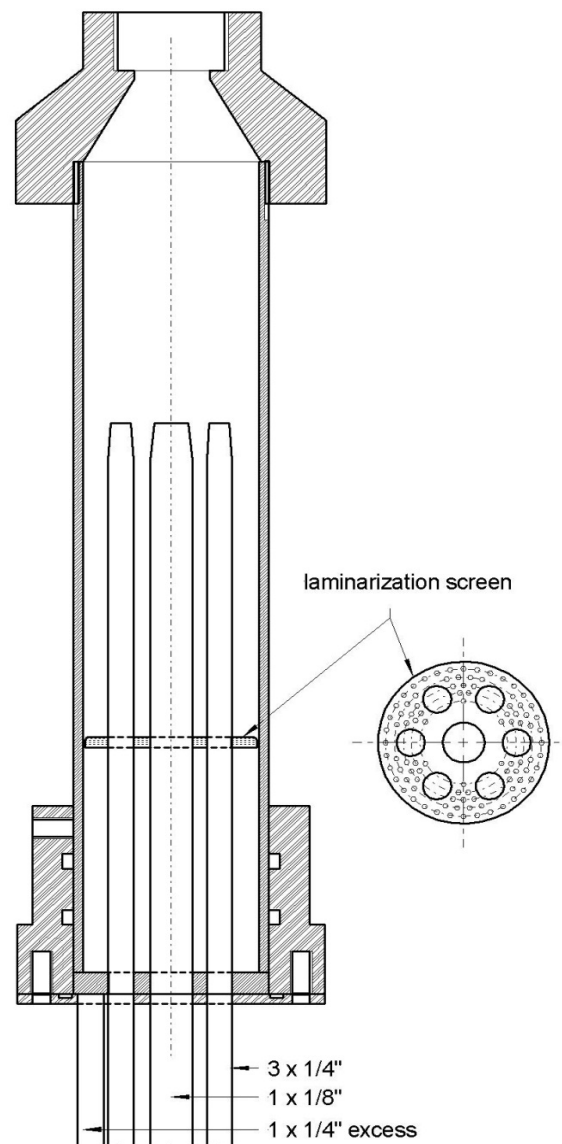
Observational networks, such as WMO/GAW, recommend an upper cut point of 10  $\mu\text{m}$  at ambient conditions (WMO GAW Report No. 153). The rationale is that particles larger than 10  $\mu\text{m}$  tend to be of local origin and are, thus, not representative for the regional-scale aerosol and its impact on climate effects. TSP (Total Suspended Matter) inlets, in contrast, turn out to be sensitive towards wind speed and cannot provide representative samples of larger particles. To obtain additional sizing information, aerodynamic size cuts of 2.5  $\mu\text{m}$  (ambient conditions) or 1  $\mu\text{m}$  (dry conditions) are recommended by WMO/GAW to distinguish fine and coarse particles. The recommendations of the WMO GAW Report No. 153 were also adopted by the European Monitoring and Evaluation Programme (EMEP), the European Supersites for Atmospheric Aerosol Research (EUSAAR) and Aerosols, Clouds, and Trace gases Research InfraStructure Network (ACTRIS).



### 2.3 Tubing and flow splitters

Inside the measurement station, the aerosol flow is usually distributed among several instruments. For aerosol particles, care should be taken with the choice of the tubing and the design of flow distribution devices. Pipes conducting aerosol should be manufactured from metal, preferably stainless steel. It is vital for the sampling of particles that the pipes are made of conductive material, and electrically grounded. Otherwise, static charges may remove significant portions of the aerosol to be sampled. Short pieces of tubing might be replaced by conductive silicone tubing, which is elastic and conducting at the same time. A perfect inlet installation also avoids sources of turbulence (bends, connectors) as best as possible (turbulence enhances particle losses due to diffusion) and keeps the sampling lines as short as possible.

Figure 2.2 illustrates a custom-designed isokinetic flow splitter in which the sample flow velocity is near the flow velocity of the main flow. Another key feature of the splitter is that a sample is removed from the core of the main aerosol flow rather than from streamlines near the wall of the main pipe. This principle ensures a representative sampling especially of coarse and Nano-particles.



**Figure 2.2. Example sketch for an isokinetic flow splitter**

## 2.4 Sample drying

The choice of dry air versus ambient RH cuts in sampling is an issue deserving more discussion. Ideally, the ambient cut is preferred because it disturbs the aerosol least and prevents volatilization of semi-volatile constituents. It is, however, very difficult to ensure that RH in the sampler is maintained at ambient RH during sampling. Dry cut sampling maintains the RH at a sufficiently low range that hygroscopic growth effects are minimized. The end results may be combined with ambient RH measurements and hygroscopic growth factors (obtained in special measurement campaigns or estimated from chemical composition) to derive the ambient aerosol size. Because of the control on sampling RH, dry cut is preferred over wet cut. It should be kept in mind, however, that dry cut has its own problems too, particularly for particulate semi-volatile components. The 1.0  $\mu\text{m}$  dry air cut is recommended over the 2.5  $\mu\text{m}$  cut at the ambient relative humidity (RH), since particles smaller than these sizes are usually strongly hygroscopic and the size segregation must not depend on RH. It is achieved by lowering the relative humidity to <40% prior to separating the particles with impactors or cyclones. The preferred methods for reducing the relative humidity are to remove water vapour with a diffusion or membrane dryer, alternatively to reduce the dewpoint temperature by diluting the sample with filtered, dry air. An alternative, but less preferable, method is to reduce the RH to 40% by modest heating to a temperature not to exceed 40°C (to minimize loss of semi-volatile species); as a general rule of thumb, a temperature increase of 10°C will reduce the RH by about half, so more than 10°C heating will rarely be needed. If heating is used, care must be taken to insulate the connecting tubing and affected instruments from the cooler laboratory air.

## 2.5 General aspects of particle motion

The design of an aerosol inlet can be customized by qualified engineers to fit the sampling requirements, based on the principles described below. However, these inlets must be well characterized in terms of the particle cut-off and aerosol transmission efficiencies at selected aerosol sizes spanning the size range of interest. Specifications of these custom inlets should be submitted to WMO/GAW WCCAP for review, to avoid serious sampling discrepancies between stations in the GAW network. Alternatively, commercially available inlets, whose particle cut-off and transmission efficiencies have been well characterized can be used for this purpose. Those wishing to establish GAW aerosol measurements are advised to seek advice from the WCCAP.

The main challenge when transporting the aerosol to collectors and aerosol measuring instrumentation is to avoid particles losses. Particle loss mechanisms are size-dependending and are generally caused by particle diffusion, impaction, and sedimentation. Generally, losses due to particle diffusion are critical for ultrafine particles smaller than 0.1  $\mu\text{m}$ . In contrast, particle losses due to sedimentation and impaction are related to supermicrometer particles in horizontal and sloping pipes as well as bends. The configuration of the whole sampling configuration and the regime of the main air flow are strongly dependent on the purpose of the observational network.

The regime of an air flow in a pipe, laminar vs. turbulent, is characterized by its Reynolds Number (Re). A flow in a pipe is laminar up to a Reynolds Number of approximately 2000. Above this value, the flow becomes gradually more and more turbulent. The Reynolds Number of the flow can be determined by

$$\text{Re}_{\text{flow}} = \frac{\rho_G \cdot u_{\text{flow}} \cdot D_{\text{pipe}}}{\eta_G}$$

Hereby is  $\rho_G$  the gas density,  $u_{\text{flow}}$  the flow velocity,  $D_{\text{pipe}}$  the inner diameter of the pipe, and  $\eta_G$  the gas viscosity.

The inertia of a particle in a flow is characterized by its Stokes Number  $Stk$ .

$$Stk = \frac{\tau \cdot u_{\text{flow}}}{D_{\text{pipe}}}$$

with

$$\tau = \frac{\rho_p \cdot D_p^2 \cdot C_C}{18\eta_G}$$

Hereby is  $\tau$  the relaxation time of the particle,  $u_{\text{flow}}$  the flow velocity,  $D_{\text{pipe}}$  the inner diameter of the pipe,  $\rho_p$  the particle density,  $D_p$  the particle diameter,  $C_C$  the Cunningham correction factor, and  $\eta_G$  the gas viscosity.

### 2.5.1 Laminar flow sampling configuration

Generally, a laminar aerosol sampling is recommended in the GAW network to minimize particle losses due to diffusion and inertia over a wide size range, especially for ultrafine and coarse mode particles. Furthermore, the pressure drop from the inlet to the instruments can be kept in the range of few hPa. Minimum losses due to particle diffusion in a laminar flow can be achieved by keeping the length of the pipe as short as possible and the flow rate as high as possible. Particle losses of supermicrometer particles can be minimized by avoiding bends or horizontally orientated sampling pipes.

To design a laminar sampling configuration, the size-dependent particle penetration can be calculated (Hinds, 1982) by:

$$P = 1 - 5.5\mu^{2/3} + 3.77\mu$$

For  $\mu < 0.007$

$$P = 0.819 \cdot \exp(-11.5\mu) + 0.0975 \cdot \exp(-70.1\mu) + 0.0325 \cdot \exp(-179\mu)$$

For  $\mu > 0.007$

$$\mu = \frac{D \cdot L_{\text{pipe}}}{Q}$$

Hereby,  $D$  is the particle diffusion coefficient,  $L_{\text{pipe}}$  the length of the pipe, and  $Q$  the volume flow rate.

In cases that bends cannot be avoided in the sampling pipe, the size-dependent particle penetration can be calculated by

$$P = 1 - Stk \cdot \frac{\theta^\circ}{180^\circ} \pi$$

Hereby,  $\theta$  is the angle of the bend.

Size-dependent losses due to sedimentation of supermicrometer particles in horizontal or sloping pipes can be calculated by

$$P = 1 - \frac{2}{\pi} \left[ 2\kappa \sqrt{1 - \kappa^{2/3}} - \kappa^{1/3} \sqrt{1 - \kappa^{2/3}} + \arcsin(\kappa^{1/3}) \right]$$

with

$$\begin{aligned} \kappa &= \varepsilon \cdot \sin(\theta) \\ \varepsilon &= \frac{3}{4} Z \\ Z &= \frac{L_{\text{pipe}}}{D_{\text{pipe}}} \cdot \frac{u_s}{\bar{u}_{\text{flow}}} \end{aligned}$$

Hereby,  $L_{\text{pipe}}$  is the length of the pipe,  $D_{\text{pipe}}$  the inner diameter of the pipe,  $u_s$  the sedimentation velocity,  $\bar{u}_{\text{flow}}$  the mean flow velocity, and  $\theta$  the angle of the pipe against the horizontal plain.

### 2.5.2 Turbulent flow sampling configuration

High-flow turbulent aerosol sampling configurations may be used at monitoring sites with a primary focus on particles that are responsible for radiative climate forcing. To design a turbulent sampling configuration, the size-dependent particle penetration can be calculated using the below equations. The size-dependent particle losses due to diffusion can be estimated to:

$$\delta = \frac{28.5 D_{\text{pipe}} \cdot D^{1/4}}{\text{Re}_{\text{flow}}^{7/8} (\eta_G / \rho_G)^{1/4}}$$

Hereby is  $D$  the diffusion coefficient,  $D_{\text{pipe}}$  the inner diameter of the pipe,  $\eta_G$  the gas viscosity,  $\rho_G$  the gas density, and  $\text{Re}_{\text{flow}}$  the Reynolds number of the flow. The particle size-dependent deposition velocity  $u_{\text{dep}}$  to the wall is then given to:

$$u_{\text{dep}} = \frac{D}{\delta}$$

The particle size-dependent penetration can be calculated to:

$$u_{\text{dep}} = \frac{D}{\delta}$$

$$P = \exp\left(\frac{-4 \cdot u_{\text{dep}} \cdot L_{\text{pipe}}}{D_{\text{pipe}} \cdot \bar{u}_{\text{flow}}}\right)$$

Hereby is  $\bar{u}_{\text{flow}}$  the mean flow velocity and  $L_{\text{pipe}}$  the length of the pipe. The particle penetration through a bend depends on the Stokes Number and curvature of the bend. The size-dependent particle penetration can be approximated by

$$P = \exp\left(\frac{-4 \cdot u_{\text{dep}} \cdot L_{\text{pipe}}}{D_{\text{pipe}} \cdot \bar{u}_{\text{flow}}}\right)$$

$$P = \exp\left(-2.823 \cdot Stk \frac{\theta^\circ}{180^\circ} \pi\right)$$

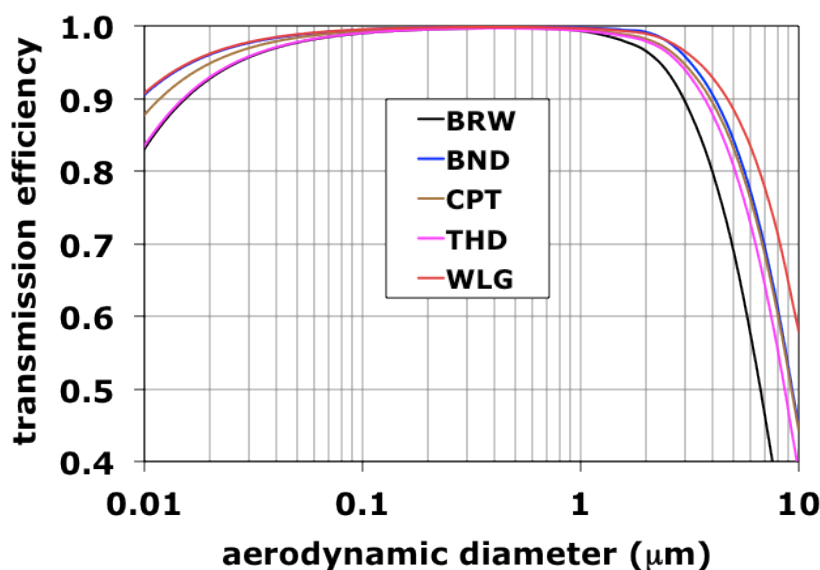
The penetration in a horizontally oriented pipe due to sedimentation is described by

$$P = \exp\left(-4Z \cdot \cos\left(\frac{\theta^\circ}{180^\circ} \pi\right)\right)$$

**Example of a sampling configuration with a turbulent flow:**

This sampling configuration with a turbulent flow is used at NOAA's long-term aerosol monitoring stations and is designed to provide up to 120 l/min of conditioned aerosol flow from a shared inlet to analysers and sample collection devices. This design is optimized to provide quantitative measurements on particles in the size range 0.02-2  $\mu\text{m}$  aerodynamic diameter, with an additional goal of achieving 50% collection of particles up to 10  $\mu\text{m}$ . The design can support multiple analysers and filter samplers that need flow rates up to 30 l/min each to be operated in parallel.

The tradeoffs required to achieve these design goals include turbulent flow conditions in the sample lines, sub-isokinetic conditions at transitions to smaller diameter sample lines, and non-isoaxial conditions in which the flow is split into four separate lines. In spite of these tradeoffs, calculations of particle losses due to turbulent diffusion, impaction, and sedimentation show that the design criterion for size-dependent sampling efficiency is met in many implementations of the system as shown in Figure 2.3.



**Figure 2.3. Calculated particle losses in the NOAA inlets as function of the aerodynamic particle diameter**

The design of the inlet can be briefly summarized to:

- A 20 cm diameter PVC sampling stack is supported by a triangular meteorological tower, and generally extends 10 m above adjacent structures.
- An inverted stainless steel pot is used as a rain hat.
- A 5 cm diameter heated stainless steel tube extracts 150 l/min aerosol sample flow with a  $Re=4500$  from the centre of the 1000 l/min main stack flow with  $Re=7500$ .
- The heater is controlled by a downstream relative humidity sensor to maintain the RH at no more than 40%, with a thermostat disabling the heater if the air temperature reaches 40°C.
- Air leaving the heated tube is split into four analytical sample lines (1.9 cm diameter, 30 l/min each,  $Re=2700$ ) and one bypass line (30 l/min).
- The sample lines are at an angle of 3.75° from the axis of the heated sample tube.
- The 1.9 cm diameter sample lines are made of stainless steel and/or conductive silicone tubing of various lengths, depending on the particular station.

Advantages and disadvantages of this turbulent sampling configuration are following:

- High aerosol flow rate
- Short residence time in sampling system
- Less losses due to sedimentation in horizontal pipes
- Increased losses of ultrafine particles due to enhanced diffusion
- Increased losses of coarse particles due to enhanced impaction
- Limited ability to actively dry the aerosol flow

## 2.6 Integrated aerosol sampling and local contamination

Every GAW Global and Regional site should be chosen to avoid local contamination to the greatest extent possible. Continuous measurements should be flagged when local contamination is present. However, integrated samples (e.g. filter samples) may need special controls to exclude locally-contaminated air in order to obtain samples that are representative of a wider area. This can be accomplished by turning off the pumps, or by-passing the integrated sampler during conditions that lead to local pollution at the site, e.g. when the wind is from a direction with known, local sources.

## 2.7 Sampling system integrity

The integrity of the sample delivery system should be checked on a monthly basis. This can be done by placing a filter on the main aerosol sampling inlet, or ahead of individual instruments, and recording the response of the continuous aerosol analysers. Changes over time in instrument response to filtered air indicate that leaks may have developed in the system, and that corrective action is necessary. The CN concentration (Chapter 5) is the most sensitive indicator of system integrity.

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## CHAPTER 3. AEROSOL CHEMICAL MEASUREMENTS AT GAW STATIONS

### 3.1 Introduction

The primary goals of aerosol chemical measurements at GAW stations are: i) to determine long-term trends locally and, taken collectively, in global distribution; ii) assess the impact of aerosol particles on regional and global climate; iii) monitor regional air quality. In addition, long-term measurements of the chemical size distribution of aerosol particles can be used to evaluate and improve aerosol chemical transport models used in air quality forecast and climate models.

### 3.2 Critical issues for a GAW station for aerosol chemical monitoring

Due to the complexity of different aerosol types, a successful network programme must address numerous issues in chemical measurements and analysis. Several guiding principles are recommended for chemical sampling and analysis in the GAW aerosol network:

- 1) Simplicity and ruggedness of the sampling, measurement, and analysis system. Recommended techniques are to be implemented at GAW network stations, therefore, they should favour a low level of technical expertise as well as low levels of maintenance to enhance the success of the programme.
- 2) Wide availability of the measurement technique. Advanced systems are used by atmospheric scientists worldwide to provide information on particle chemical composition but high costs and need for advanced expertise are clear limitations for use in the GAW network.
- 3) Use of a standardized aerosol filter medium. This will ensure uniformity and comparability among the stations. Quality assurance and quality control expertise or even resources can be shared among the stations.
- 4) Minimize hardware and training costs. The lower the capital costs are, the more likely it is that long-term measurements of quality will be obtained globally.

Thus, the type and number of analyses recommended here are, unless otherwise stated, the minimum that is considered consistent with the scientific objectives of the GAW network. If financial constraints dictate cutbacks, it is recommended that the cutbacks be achieved through a reduction in the number of samples that are analysed rather than a reduction in the number of chemical species.

### 3.3 Recommended chemical sampling techniques and analysis

#### 3.3.1 Sampling media and methods

For mass measurements and chemical analyses, except organic carbon, filtration with a Teflon filter is recommended for aerosol collection (Section 3.3.5.1). There are several reasons for this choice. These include:

- 1) The extensive use of this filtration medium in various existing measurement networks.
- 2) Its commercial availability.
- 3) The efficiency of aerosol particle collection (at commonly used face velocities, >99% of particles with 5 nm diameter or greater will be trapped on Teflon filters of <1  $\mu\text{m}$  pore size).
- 4) Chemical inertness (it absorbs minimal amounts of water vapour and reactive gases making it suitable for many types of chemical analyses as well as gravimetric mass concentration and particle light absorption measurements).
- 5) Low chemical content (this results in lower atmospheric detection limits; the exception is nitrate; current filters appear to have varying levels of blanks - a point for further discussion below).



A filter diameter of 47 mm diameter is recommended as a standard size, facilitating the intercomparison of data and adaptation of common QA/QC procedures. It is the diameter commonly used in many existing monitoring networks. However, this does not prevent the use of other sizes. Indeed, different geometry of filter holders may be used as long as the size cut is maintained.

Quartz fibre filters should be used for organic carbon measurements. This is the only exception to the Teflon filter since the currently accepted analytical method for organic carbon, thermal desorption and evolution, requires such a specific filter medium. The quartz fibre filters must be fired before use, at a recommended temperature range of 850-900°C, to reduce the organic carbon content of the filters. As a QA/QC procedure, it is recommended that randomly selected filters from the fired filter batches be tested for organic carbon blanks, before the batches are used for field sampling; if organic carbon blanks exceed a set limit (such as  $2\sigma$  of the average blank values over all blank tests), then the batch of filters may be rejected for sampling. Given the evolutionary nature of the analytical technique, this recommendation should be viewed as an interim solution.

It is recommended that other types of filter media NOT be used particularly for stations starting an aerosol chemical sampling programme. For historic reasons, some of the existing stations may have used other filter medium types, such as cellulose-based filter media and continue to do so. These stations should consider switching to Teflon, but should have an overlap period of at least two years for the two measurements. Given the long-term objectives of the GAW programme, any changes in the monitoring record due to changes in sampling/analytical techniques must be carefully documented. A transition period of at least two years will allow these changes to be accounted for over different seasons. If, on the other hand, ongoing measurement programmes wish to continue sampling practices, a careful study must be conducted to determine whether the recommended GAW chemical measurements are compromised.

The filtration method has potential interferences, particularly for semivolatile chemical species. Interpretation of results must account for these interferences. For non-volatile species, such as sea salt and mineral dust, the interferences are negligible, because either there is no gas phase equivalent for adsorption onto the filters, or the filters do not absorb the gases, or these components are stable and do not volatilize. For semivolatile chemical species, such as ammonium nitrate, and some organic carbon species (e.g. light polycyclic aromatic hydrocarbons), interference may come from both the adsorption of gases on the filters and particle volatilization on filters during sampling. Adsorption depends on the type of filter material as well as environmental conditions, whereas volatilization is more dependent on environmental variables and the inherent properties of the filters (such as pressure drop across the filter under normal sampling conditions) other than the filter composition.

The face velocity at which air is drawn through a filter can affect both the adsorption and volatilization properties of particles and gases. For sulfate, volatilization does not occur; but under some special situations, such as a marine or coastal site where particles are expected to be alkaline, adsorption of  $\text{SO}_2$  onto deposited particles and further conversion to sulfate may happen, leading to positive interference. In quartz fibre filter samplings for organic carbon, the positive bias (adsorption) has been found to be much larger than the negative bias (particle volatilization) (Turpin et al., 1994). In contrast, ammonium nitrate is particularly susceptible to volatilization from filters. Quantifying these artifacts during sampling is necessary in order to obtain accurate measurements of the volatile compounds (and thus implicitly also PM). To assess the extent of interference problems, a denuder-filterpack combination may be used, particularly for the semi-volatile components. Other filter media may be used for specific measurement objectives.

In addition to filtration, impaction may be used in a programme covering the comprehensive list of measurements in Table 1.1. This has been most commonly used in studies of particle mass size distribution. In cascade impactor sampling, different collection substrates have been used to serve different purposes. For example, aluminium foils have been used for mass and

particulate carbon size distribution measurements, Teflon filters for chemical component size distribution, and polycarbonate filters for elemental/metal size distributions. In all cascade impactor sampling, wall losses and bounce-off are known problems and steps should be taken to minimize them. Commonly known techniques to prevent particle bouncing include humidifying the air stream to force aerosol deliquescence before impaction, and application of grease over the impaction surface. Similar to filter sampling, gas adsorption (positive artifact) and particle volatilization (negative artifact) may occur during cascade impactor sampling, particularly for low pressure stages.

While the GAW guidelines do not rule out cascade impactors from being used on a long-term basis, it is recommended that these be conducted only on an intermittent basis (Table 1.1) to help characterize the long-term continuous filtration measurement. The same applies to denuder-filterpack measurement. If carried out, these measurements will create a large workload not only for laboratory chemical analysis, but also for the sampling and handling as well. Furthermore, specific QA/QC plans, separate from those for regular filter sampling, must be in place. The station will probably also be on its own for auditing and calibration purposes because cascade impactor and/or denuder-filterpack sampling are not GAW core variable requirements. These add up to significant financial and resource requirements that few stations can sustain in the long-term.

### **3.3.2 Sampling setup for aerosol chemical analysis**

For the routine long-term aerosol measurements at GAW stations, it is recommended that up to three sets of 47 mm diameter filters should be collected in parallel. If financial constraints are limiting, the priorities for filter sampling are: a) Teflon filters for gravimetric and ionic analyses; b) quartz-fibre filters for carbonaceous aerosol analyses; c) Teflon filters for elemental analyses. Each set would consist, ideally, of two filters, one for total mass below 10  $\mu\text{m}$  diameter and one for the fine fraction. The separation would be achieved by running the filters behind the size-selective inlets as discussed in Section 2.2.

For simplicity, it is suggested that a differencing technique be utilized to separate the coarse fraction from the fine fraction. Specifically, one filter should be run behind the 10  $\mu\text{m}$  diameter cut inlet. A parallel filter would be run behind the inlet suitable for the fine fraction (i.e. 2.5  $\mu\text{m}$  diameter at ambient RH or 1.0  $\mu\text{m}$  in dry air; see Section 2.2 for details). While the second filter will yield the fine fraction, the difference between the two filters will then yield the coarse fraction.

### **3.3.3 Flow measurements**

Because the final measurement results are expressed in terms of particle mass concentration (particle mass per unit air volume), an accurate air volume for each aerosol particle sample must be determined. In addition, there probably will be cases in future data analyses where mixing ratios, instead of air concentrations, are needed. This requires that ambient temperature and pressure are recorded for the conversion of units. The air volume should be reported for the recommended standard temperature and pressure of 273.15 K and 101.32 kPa, respectively (Section 2.6).

Air volume for each sample can be determined by integrating air flow rate over the sampling duration. There are different methods of determining the air flow rates. The most common method uses a calibrated in-line mass flow meter or mass flow controller. These devices measure the mass of air that passes through a sensor (usually by way of heat conductance measurements). The sensor should be well calibrated against known standards periodically. Mass flow meters and controllers are normally used for low to medium flow rates. For the recommended 47 mm Teflon filters, these devices are appropriate. Other flow rate measurement systems may be used, provided that they are calibrated for the operating

conditions. For example, flow rates can also be determined by measuring the pressure drop across an orifice, coupled with temperature measurements. It is explicitly recommended that rotameters not be used for flow measurements at GAW stations.

For the recommended 47 mm Teflon filter, a flow rate of 15 to 30 L min<sup>-1</sup> is suggested. For each sample, the flow rate should be recorded continuously on a central data collection system and properly archived. Although recommended for the 47 mm Teflon filters, it should be noted that the flow rate need not be the same at all GAW stations, as it depends on the particular sampling device, the sampling inlet and sensitivity of the chemical analysis methods. In particular, if other configurations of the filter sampling are set up to collect aerosols, such as dichotomous high volume samplers, the flow rates can be substantially higher (e.g. over 1000 L min<sup>-1</sup>). After a period of one year, the suggested flow rate should be assessed and even adjusted for each station and varied to obtain the optimum number of successful samples and optimum sample load on the filters. In this case, flow rates may need to be controlled at the new rates.

### **3.3.4 Sampling frequency**

Several issues arise in connection with aerosol particle sampling for chemical analysis; issues that are interrelated and of practical importance, namely, sampling frequency and sample flow rate. One must consider the time resolution necessary to address the scientific questions that the GAW network is supposed to resolve, and balance this against available flow rates and expected aerosol particle mass loadings on each sample. Simply put, the issue is about the detectability of the chemical species on each filter by the analytical method.

It may not be possible to analyse all daily samples for chemical concentration. If due to financial constraints not all samples can be analysed, the following alternatives should be considered: i) sample every day of the week and archive every other sample, hence effectively reducing the sample analysis by half; or ii) sample every day of the week and only analyse one sample every week; or iii) take a daily sample every 6th day and analyse it. These 3 alternatives are preferred to a weekly integrated sample which is difficult to relate to meteorological transport conditions. In all cases, unanalysed samples should be archived in separate, clean, dry, cool containers for possible later analysis in case of unusual events. To ensure the quality of the sampling and subsequent handling procedures, 5-10% of the samples should consist of field blanks.

The above are general recommendations, however, special exceptions can be made. For example, for stations where substantial diurnal cycles take place due to various factors (meteorology, chemistry, radiation, etc.), it is recommended that a sampling interval of 12 hours be used for the sampling programme, with the sample change timed appropriately. Conversely, stations in pristine locations may require 48 hours or more (up to a week) to collect sufficient sample volume for analysis.

Whether the sampled air volume is too small or too large should be reviewed at each site in the first year. The air flow rates and inlets may need re-adjustment. If overloading of the filters occurs due to excessively high air concentrations, the flow rate should be decreased. If underloading occurs due to very low air concentrations the sampling flow rate should be increased. A change of inlet may prove to be technically and financially challenging. Alternatively, the lab analytical protocols can be changed, such as dilution or concentration before analysis with proper QA/QC documentation, to handle the overloading/underloading of samples and to achieve the optimal analytical sensitivity.

### **3.3.5 Recommended analyses and considerations**

For each GAW station performing aerosol measurements, a list of core aerosol particle chemical analysis is strongly recommended: i) mass concentration; ii) major ionic species; iii) mineral dust; iv) carbonaceous components. The analytical techniques described below have proven to be capable of accounting for 85 to 90% of the measured mass and achieve an

adequate aerosol mass closure. In addition to the chemical species above, individual stations may wish to consider additional analyses, such as tracer components. These analyses are discussed in detail below.

### 3.3.5.1 Mass

The mass concentration of atmospheric aerosol particles is clearly a fundamental parameter in the GAW measurement programme. It is recommended that this be done gravimetrically on Teflon filters. The aerosol particle mass concentration in air is commonly determined from the net aerosol particle mass on a filter at a recommended relative humidity (RH) range, divided by the volume of air sampled (Chow, 1995; Willeke and Baron, 1993; Baron and Willeke, 2001; Lodge, 1988). It is expressed in units of  $\mu\text{g m}^{-3}$ , where the volume is related to standard temperature and pressure. There are also continuous instruments for mass measurements as discussed in a separate section below.

While simple in appearance, there are many practical issues related to gravimetric measurements on Teflon filters (or any other collection medium). These arise from 4 areas: i) the equilibration of the aerosol particle samples with the microenvironment of the balance; ii) the static electric charge on the filters; iii) the sensitivity of the balance; iv) the changes in filter buoyancy due to changes in air density. Equilibrium of the sample with the microenvironment is the most critical issue. This is because soluble aerosol particles are hydrophilic and thus attract water. The water content can change substantially with changes in ambient temperature (T) and thus in relative humidity (RH). Therefore, it is important to maintain a constant set of micro-environmental conditions for weighing the aerosol particle samples on filters and minimize the changes in both T and RH.

The net particle mass on the filter sample is determined from the weight difference of the filter before and after sampling. To maintain a constant T and RH, weighing must be done with a balance in a T and RH-controlled environment. Prior to weighing, the filters should be equilibrated at the controlled constant T and RH for 24 hours. For the GAW network, a constant temperature and RH of  $20^\circ\text{C} \pm 1^\circ\text{C}$  and  $20\% \pm 5\%$  are recommended following reference methods applied by air monitoring networks.

While balances with  $\leq 100 \mu\text{g}$  sensitivities are adequate for weighing high-volume samples where 10s of milligrams of net mass are expected, electro-balances with sensitivities below  $1 \mu\text{g}$  are required for the recommended Teflon filter collection at the GAW stations. The same applies to aerosol particle samples collected using other low volume devices (air flow rate  $\leq 30 \text{ L min}^{-1}$ ), especially if cascade impactors are used. Calibration of the balance must be carried out using standards of similar weights at the same microenvironment as the samples. The standards must be traceable to primary or secondary standards of metrology services affiliated to BMPI (Bureau International des Poids et Mesures).

Static electric charge on filters is especially significant for filters with high dielectric constants such as Teflon. Charge can accumulate on filters during the manufacturing process as well as the sampling and handling processes. The charges can result in handling difficulties, enhanced or diminished particle collection, and weighing errors. Weighing error is magnified when the collected mass is small. Under the recommended GAW sampling protocol, the collected aerosol particle mass is expected to be in the range of 10s to 100s of  $\mu\text{g}$ . The sensitivity of the balance must be sufficient to accurately determine this. To remove any electric charge, the filter should be exposed to a corona discharge device or a low-level radioactive source such as Po-210 or Am-241 prior to and during weighing.

Accurate gravimetric particle mass determinations require ideally the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapour and other gases. Teflon filters, recommended for the GAW aerosol chemistry programme, meet these mass measurement requirements reasonably well even though the dielectric constants are high. Although not recommended for use with the GAW programme, several

other types of filters also meet the requirements reasonably well, including cellulose esters, and polycarbonate, which may still be in use in established GAW stations. On the other hand, cellulose fibre filters (e.g. Whatman 41) are not recommended for mass determination, because of the large and irreversible uptake of water vapour. Quartz or glass fibre filters may be used, where the potential loss of filter substrate material during handling is insignificant compared to the mass loadings.

These precautions notwithstanding, virtually all types of filters have a tendency to experience small changes in weight after they have been sent to the field and back without any sample on them. Therefore, along with the filters that are used for sampling, blank filters must be taken and handled in the same way as the real samples. The net mass (either negative or positive) on the blanks must be determined and used to correct the results of the samples. In addition, special care must be taken when the filters are weighed; these filters are expected to be re-analysed as further discussed below.

Semi-continuous instruments are also available and may be used for the determination of the aerosol particle mass concentration provided that their equivalence with gravimetric methods has been established. These types of instruments are further discussed in Section 3.5.

### 3.3.5.2 *Ionic species in aerosols*

It is recommended for the GAW stations that chemical analyses be done for at least a minimum set of major ionic species in aerosols. This set includes sulfate, nitrate, chloride, sodium, ammonium, potassium, magnesium, and calcium. This selection of analyses is based on the fact that analytical procedures for them have become well established. More importantly, under most atmospheric conditions, this set of ions is expected to account for a major part of the aerosol mass, and the measurements here are an important step toward mass closure of the aerosols.

These analyses should be done using ion chromatography (IC) for the most cost-effective approach. If financial resources allow it at the GAW stations, IC should be implemented across the entire GAW network to ensure uniformity and comparability. The IC technique has the advantage of chemical speciation and relatively low cost per analysis, and has matured to the degree that the sensitivities for each ionic species, cost, and maintenance are all reasonably well known. If IC is set up properly, all the recommended ionic species can be analysed in one single sample injection. For sodium, potassium, magnesium, and calcium, the analyses can be done without IC using atomic absorption spectroscopy (AAS) or inductively-coupled plasma mass spectroscopy (ICPMS). Reference methods exist for determination of specific elements collected on filters and GAW recommends following these procedures whenever possible. However, as the use of these alternative analytical techniques may introduce systematic differences amongst GAW stations, the equivalence of these alternative techniques with IC must be established and well documented.

For IC analysis, filter samples should be extracted in an appropriate amount of deionized water. A volume of 10-20 ml of deionized water is suggested for the recommended filter (47 mm Teflon) and total sample volume (approximately 30 m<sup>3</sup>). This will produce relatively high concentrations for most of the recommended ionic species, yet provide enough extract volume for all the analyses. Repeated analyses should be done on a regular basis (i.e. multiple analyses on one sample out of every five). The repeat analyses will give a good estimate of the analytical precision. Standards must be prepared to cover the concentration ranges seen in the samples. It is essential that the IC laboratory participate in round robin interlaboratory comparison programme arranged within GAW programmes in particular within the specific precipitation programme. Recommendations for data quality described in GAW Report No. 160 (Manual for the GAW precipitation chemistry programme; Guidelines, Data Quality Objectives and Standard Operating Procedures) can be extensively followed.

Additional ionic species may be analysed for targeted studies of specific processes over an extended period of time beyond the minimum set of ionic species. However, this will probably

require additional IC runs for the same sample or the use of gradient methodology. An example of such an additional species is MSA for samples collected at marine sites. MSA is an indicator of marine biogenic sulfur emissions, and changes in MSA may indicate changes in the strength and/or processes of marine biogenic sources.

The following sections are more detailed descriptions of the ionic species recommended to be measured at the GAW stations.

### **Sulfate (SO<sub>4</sub><sup>2-</sup>) and ammonium**

Sulfate (SO<sub>4</sub><sup>2-</sup>) is the most studied chemical component of all and is ubiquitous in aerosols. Non-sea salt (NSS) sulphate, determined by correcting for sea-salt sulfate using the Na<sup>+</sup>/SO<sub>4</sub><sup>2-</sup> (or Mg<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup>) ratio in seawater and Na<sup>+</sup> (or Mg<sup>2+</sup>) measurement results, dominates aerosol sulphate. NSS is one of the most dominant mass contributors to submicrometer marine aerosol particles. But in the alkaline coarse sea salt or dust aerosols, significant amounts may be found resulting from uptake of SO<sub>2</sub>. In the case of coarse sea salt aerosols, significant amounts of sea salt sulphate exist.

A second source of natural sulfate comes from mineral dust. This component may be corrected for by using the Ca<sup>2+</sup>/SO<sub>4</sub><sup>2-</sup> ratio in mineral dust (Henning et al., 2003).

For SO<sub>4</sub><sup>2-</sup>, IC method has a high sensitivity and few problems. The same is true for ammonium ions. However, it should be cautioned that acidity titration by ammonia during filter handling processes is likely, and that special care must be taken in the handling processes to avoid contamination from this titration. This requires that stringent SOPs be established, for example, handling filters in an ammonia free microenvironment (such as a scrubbed glovebox), which are followed for the filter handling in both the field and the laboratories. Such procedures are a requirement for reliable ammonium measurements.

### **Nitrate and ammonium**

Nitric acid vapour is formed in the atmosphere from the oxidation of NO/NO<sub>2</sub>. Its reaction with alkaline components in aerosol particles leads to particulate nitrate. It can also co-condense with ammonia vapour to form ammonium nitrate and add mass to particles. However, the nitric acid and ammonia vapours should be in equilibrium with the particle ammonium nitrate. Alternatively, aerosol nitrate may be formed directly from reactions of various nitrogen oxides on alkaline particles without going through the gas phase nitric acid as the first step.

Because nitrate can form stable mixed salts with SO<sub>4</sub><sup>2-</sup> salts, it can coexist with SO<sub>4</sub><sup>2-</sup> in the fine aerosol fraction, especially in the accumulation mode. On the other hand, the reaction of nitric acid or nitrogen oxides with alkaline particles, mostly in the coarse fraction, will lead to coarse mode nitrate (Henning et al., 2003). In both coarse mode and the accumulation code, nitrate can make a significant contribution to the aerosol mass.

In regions with predominantly ammonium nitrate and low levels of other anions, there are potential problems in sampling of nitrates arising from the volatilization of ammonium nitrate from the filters. In these situations, caution should be exercised in interpretation of data. Ancillary measurements using Teflon/Nylon filter pack samples with appropriate elimination of the gaseous nitric acid with a denuder are then recommended.

### **Sea salt ionic components**

Sea salt ionic components are important for aerosol particles, particularly in the coarse mode. Over the oceans, bubble bursting generates coarse and fine sea salt particles. Sea salt particles dominate the mass of the coarse mode over the oceans and coastal areas, contributing to particle light scattering in these regions. Measurements of sea salt components in aerosol particles are less prone to sampling errors. These components include the cations, sodium and magnesium. Chloride is also part of the sea salt components. However, because of the reaction of sea salt particles with acidic gases such as SO<sub>2</sub> and HNO<sub>3</sub>, the chloride ion may be lost from the sea salt particles. Because the cations are non-volatile, they are not

expected to experience the same sampling problems as nitrate/ammonium. Furthermore, the blank levels of these ions on Teflon filters are stable and low.

It is recommended that the Teflon filter samples from the GAW stations be analysed for the cations using the IC technique. This technique performs the analysis well and has high sensitivities for the recommended cations, yielding, in one analysis, all the cations along with ammonium. Separate anion analyses of the same sample will yield the chloride ion together with sulfate and nitrate, and the chloride results can be used to study the degree of acid-base reaction on the sea salt components. However, care must be taken to account for post sampling losses of chloride in the interpretation of results.

Alternatively, the sea salt components can be analysed by the destructive methods AAS, ICPMS, or the non-destructive methods such as Instrumental Neutron Activation Analysis (INAA) or Proton Induced X-ray Emission (PIXE). PIXE is a non-destructive method for species that are not volatile in a vacuum. With non-destructive methods the sample may be preserved and analysed again if handled properly. In all cases, the equivalence of these analytical methods with the IC technique should be established. In addition, the QA/QC procedures of these analytical methods must likewise be well established and documented.

### **Other ionic components**

It is worthwhile to have a little more discussion here about potassium and calcium ions. The major part of potassium in aerosols is expected to come from biomass burning, and hence its analysis in the GAW programme provides a long-term record of biomass burning. Calcium, on other hand, is expected to come mainly from mineral dust. A small fraction of both ions can be expected to come with the sea salt components. It is recommended that both cations be analysed with the IC method in the GAW programme. This does not constitute extra analyses, as both will result from the same analysis for the sea salt components sodium and magnesium ions, and hence no extra analytical effort is needed for both ions. Both ions can also be obtained using different analytical methods, such as AAS or ICPMS, but differences may arise due to different extraction procedures.

Other ionic species may be of considerable importance in assessing the sources of the main species discussed above. Organic ions, including formate, acetate, propionate, and methane sulphonate (MSA), are good examples. MSA is an indicator of the biogenic nss sulphate derived from dimethyl sulfide (DMS) and probably other biogenic sulfur compounds at oceanic sites. In remote regions, other organic anions may come from biomass burning sources. If the organic ion analysis is to be carried out, it is recommended that the Teflon filters be extracted in a sufficient quantity of solution that is enough for separate IC analyses.

Analysis for the organic ions, however, requires extra expertise in the IC technique, as it calls for an IC methodology (gradient method or two columns in series) that uses more sophisticated equipment (gradient pump or multiple columns) than that (isocratic pump) needed for the minimum analyses. MSA analysis is recommended for a GAW station in marine locations, while the organic anions are useful tracers for biomass burning in remote regions.

#### **3.3.5.3 Mineral dust**

Mineral dust particles consist of crustal material originating mostly from suspension of exposed soil by wind in arid and semi-arid areas such as desert and agricultural regions. In urban areas re-suspended road dust is a major contributor. Mineral dust particles are primarily in the coarse mode; those with diameters  $>10\mu\text{m}$  fall out rapidly due to gravitational settling, while those with smaller sizes can be transported over long distances. There is plenty of evidence of hemispheric transport of mineral dust particles, such as from Gobi and Saharan deserts, crossing the Pacific Ocean and the Atlantic Ocean, respectively. In such source regions and well downwind, mineral dust particles may dominate (depending on the season) the mass concentration of the coarse mode and to some extent also fine mode. They can impact

significantly the atmospheric energy budget through scattering and absorption of solar radiation.

Because of their stability, mineral dust particles can be sampled relatively easily without the artifacts posed by more semi-volatile aerosol components such as organics and ammonium nitrate. For GAW stations, it is recommended that a multi-elemental analysis approach be used to determine the mineral dust components. Teflon filters should be analysed for at least four of the major crustal elements Al, Si, Fe, Ti, Sc and the related elements Na, Mg, K, Ca. No specific analytical technique is recommended as there is a good selection available including PIXE, INAA, XRF, AAS and ICP-MS. These techniques usually have high sensitivities for the crustal elements. Not all techniques can provide all the required elements, and depending on availability, a combination of two or more techniques may be necessary. It is recommended that results are provided giving the elemental mass for each element and not the mass of the corresponding oxide. As mentioned previously, it is also recommended that ISO standard procedures are followed whenever available when using these techniques.

#### 3.3.5.4 *Carbonaceous materials*

Carbonaceous species are the least understood and most difficult to characterize of all aerosol particle chemical components. Total particulate carbon mass (TC) can be divided into three fractions: inorganic carbonates, organic carbon (OC), and a third fraction referred to variously as elemental carbon, equivalent black carbon (EBC), soot, or refractory carbon. Some of these terms are related to the measurement method used. When using optical methods, the particle light-absorbing component is commonly equivalent called black carbon, even though the optical method is not specific for carbon. On the other hand, thermal methods discriminate between elemental (i.e. refractory) carbon and organic carbon. For the purposes of this report, the term equivalent black carbon will be used throughout for the quantity measured by optical methods and elemental carbon (EC) for thermal methods, following the recommendations by Petzold et al. (2013).

The carbonaceous components are present in a large variety of forms and species. Over most continental areas and over some marine areas, carbonaceous aerosols are at least as important in contributing to fine mode mass as sulphate, and TC is dominated by OC (Jacobson et al., 2000). The elemental carbon and carbonates are stable primary products whereas organic carbon is highly variable in terms of physical and chemical stability. The source of elemental carbon is incomplete combustion. Carbonate is found in crustal material and seawater. Organic carbon can come from primary anthropogenic and biogenic sources as well as secondary anthropogenic and biogenic sources.

It is recommended that TC, OC and EC be measured in the GAW programme, leaving out the relatively minor and difficult inorganic carbon component and the more complicated issues of organic carbon speciation. For the sampling of particulate carbonaceous materials it is recommended to use quartz filters, pre-fired at 850-900°C for two hours, and at the same sampling frequency as the Teflon filters. No particular filter fibre size is suggested here, nor is the sampling flow rate. There are potential problems with this sampling method for organic carbon. Because many organic carbon compounds are semi-volatile, positive artifacts (the adsorption of organic gases onto the filters) and negative artifacts (volatilization of semi-volatile organic components from the aerosols) on the organic carbon can occur during sampling. The two artifacts may cancel each other to a certain degree, but measurements to date show that positive artifacts usually dominate the negative ones.

The best approach to correct for these artifacts is to use denuders, coated with materials such as an eXperimental ADsorbent (XAD) resin or activated charcoal to trap the gases first, and then sample the aerosols using two quartz filters in sequence. This, however, requires expertise that does not exist at all GAW stations and adds complexities, such as special equipment to prepare the XAD denuders, to the operation. Alternative denuder methods using other absorbing materials can also be used to address the artifacts. The recommendation



here, of using quartz filters only, should be viewed as an interim solution. It is up to the station to make a decision on whether to adopt the more complicated denuder-filterpack combination for sampling.

The quartz filter can be analysed for TC using the thermal evolution technique. The particle mass concentration of total carbon is obtained by thermal oxidation of the carbon, usually at the temperature range of 750-900°C in the presence of an oxidizing agent, into measurable carbon dioxide. Detection of the evolved carbon dioxide is done in one of two ways, either by reduction to methane in the presence of a catalyst and quantification of the methane with a flame ionization detector (FID), or by direct detection of carbon dioxide by non-dispersive infrared (NDIR) detectors.

The measurement of the TC components OC and EC is more difficult than the measurement of TC (Schmid et al., 2001). The NIOSH thermal evolution method was the first technique available to achieve OC and EC separation (NIOSH; 1999). This separation is primarily based on the thermal refractory nature of EC. At high temperatures EC can be oxidized to CO<sub>2</sub>, in an oxygen-containing atmosphere only, while OC can be volatilized in an oxygen-free atmosphere and oxidized to CO<sub>2</sub>. If the volatilization process is carried out under an oxygen-free environment, some organic materials (e.g. oxygenated organic carbon) can be charred causing a positive bias in EC determination. The charred OC may be corrected by monitoring the change of either the optical reflectance or the transmittance of the quartz filter during the heating process (e.g., NIOSH (1999); Chow et al. (2001, 2004); Cavalli et al. (2010)) or minimized by higher temperature volatilization using specific-developed thermal protocols (e.g. Huang et al., (2006)). Even so, the separation is still semi-empirical because the temperature crossover point from one fraction to the other depends on various factors (e.g. laser sensitivity and stability, temperature calibration and Helium gas purity etc.). In addition, the correction for charring is based on assumptions which may not be true. Thus, the use of various optical-thermal/thermal protocols may lead to different results for OC and EC. These uncertainties notwithstanding, temperature-controlled thermal evolution (with or without laser optical monitoring) is still the most accepted method for OC and EC analysis in the field.

Further refinements to the NIOSH method have led to several protocols now in use by monitoring networks. The IMPROVE\_A protocol (Chow et al., 2001, 2004, 2007) is commonly used in North American monitoring networks. EUSAAR-2 (Cavalli et al., 2010) is the standard protocol in the EMEP network in Europe. EnCan-total-900 is the thermal method used in the Canadian Aerosol Baseline Measurements network (Huang et al., 2006). Other NIOSH-like protocols have also been used in long-term observations (e.g. Husain et al., 2008, Dutkiewicz et al., 2014). Large OC and EC datasets have been obtained around the world via different networks using these thermal separation protocols. To facilitate data submission to the GAW WDCA from existing network observations and to maximize the scientific value of these data, GAW WDCA will accept data with clear descriptions of, or references to, the OC and EC separation protocols. For new GAW stations planning on and starting aerosol OC and EC measurements, it is recommended that the well documented and researched protocols of IMPROVE\_A, EUSAAR-2, or EnCan-total-900 be adopted for use. It should be noted that this recommendation does not exclude other protocols from being adopted or developed, but the burden of providing compatibility documentation of such protocols will be the responsibility of the stations.

To ensure data compatibility across the GAW network and contributing networks, there is a strong need to develop mechanisms for assessing data comparability of OC and EC measurements using different thermal methods at different networks, as well as the consistency of the data comparability over time. The mechanisms could include:

- Long-term intercomparison of filter samples at various locations (assuming influenced by various types of sources) including regular inter-continent comparisons whenever regional networks are applying different protocols.
- Development of a reference materials for EC and regular intercomparison of measurement methods using reference materials for instrument calibration of OC and

EC fractions, ensuring that measurements by individual instruments/methods are traceable to the first principle (e.g. gravimetric approach) and are consistent over a long period of time (e.g. decadal scales).

It is strongly recommended that GAW OC and EC measurement laboratories participate in such inter-laboratory comparisons whenever they are conducted. Laboratories should submit OC and EC data to WDCA along with the results on data comparability whenever they are available.

Other techniques have been used for the determination of OC in aerosol particles such as the non-destructive technique PESA (Proton Elastic Scattering Analysis). However, we consider that giving the limited use of other techniques, they cannot be recommended in the network. A general recommendation however is that whenever an alternative approach for OC determination at a GAW station is proposed, a periodic determination of OC using the thermal method is conducted so that results can be compared.

All these measurements yield a value for the carbon concentration. For a mass balance, heteroatoms included in the carbonaceous compounds need to be taken into account as well. The factor to calculate the total mass of organic carbon differs for different species. It is 1.9 for water soluble organic carbon (Krivacsy et al., 2001), and probably around 1.2 for water insoluble organic carbon. Water soluble organic carbon is typically 40 to 50% of the total carbon (except for urban sites, where it can be as low as 10%). Thus, the usual correction factor used for total OC (1.4) is on the low side (with the possible exception of urban sites). For comparison, Turpin and Lim (2001) give even higher conversion factors, with  $1.6 \pm 0.2$  for urban aerosols and  $2.1 \pm 0.2$  for aged (non-urban aerosols).

### **Equivalent black carbon (EBC) mass derived from optical measurements**

The optical method for estimating black carbon mass involves measuring the change in optical transmission of a deposit of particles on a filter (absorption) and applying a site-specific and instrument-type-specific mass absorption efficiency to derive an equivalent black carbon (EBC) mass. The recommended method for measurement of the aerosol light absorption coefficient at GAW stations is described in detail in section 4.3. Two key assumptions are required to derive the EBC mass concentration from light absorption measurements: i) black carbon is the only species responsible for the aerosol light absorption and ii) the sampled black carbon has the same mass absorption efficiency as the standards used in laboratory calibrations of the absorption instrument. These assumptions can be evaluated by experimentally determining the mass absorption efficiency by simultaneously making light absorption measurements and EC measurements as described above. At sites where EC concentrations are not routinely determined on quartz-fibre filters, less frequent filter collections can be used to derive site- and season-specific values of the mass absorption efficiency. Thus, for GAW measurements of EBC, experimentally derived values of the mass absorption efficiency at a site are essential when estimating EBC mass concentration from light absorption measurements. Reporting of results on EBC mass concentrations derived from optical measurements should follow the terminologies recommended by Petzold et al. (2013).

#### *3.3.5.5 Trace components*

Trace components of aerosols are important as indicators of sources and processes. Some may have health effects. Tracers include both elemental and molecular forms. Due to cost considerations and the necessity to limit the number of samples, routine analyses of these species are not recommended at each GAW station. However, studies should be considered for assessment purposes on a case by case basis. For example, the gravimetric and optical absorption techniques are non-destructive and the filters for these methods could be archived for later multi-elemental analysis by PIXE/XRF/INAA for transition metals. When analysing for elements related to dust aerosols, many of the transition metals can also be obtained for

limited incremental costs. For example, in PIXE analysis, a long list of transition metals, including Ni, Cu, Zn, Fe, Pb, are obtained from the same analysis as for Al, Na, Mg, K, and Ca, all of the dust components.

The speciation of organic carbon can be used for source identification and apportionment. Some species have been successfully used as tracers for identification of major sources of the organic carbon (Hildemann et al., 1994; Schauer et al., 1996). Organic compounds can originate from primary sources (natural biogenic or anthropogenic) and secondary natural and anthropogenic sources. While much work has been done in urban atmospheres, little data are available from rural and remote locations such as the GAW stations. The amount of (primary) emitted carbonaceous biological material can be assessed by special methods (Matthias-Maser and Jaenicke, 1994). For example plant wax bears unique carbon preference indices (CPI).

Sampling for these organic carbon species has traditionally been done with quartz or glass fibre filters, again with the potential for artefacts formation as discussed above. There are many different chemical analysis techniques for aerosol organic compounds in aerosol OC often involving some form of liquid or gas chromatography. These methods are closely coupled with the sample handling procedures. For example, a simple procedure for thermal desorption of aerosols on quartz filters has been used for analysis of polycyclic aromatic hydrocarbons (PAHs) with GC/MS systems. To obtain more species, complicated extraction procedures must be used, typically with solvent extraction, followed by separation of the extracts into fractions with different polarities. These fractions are then analysed using different GC columns to obtain polar and non-polar compounds such as long chain alkanes and a more complete list of PAHs. The polar fraction is usually further derivatized to improve the sensitivity of the GC for the compounds, such as the long chain acids. Systematic and long-term comprehensive measurements such as these are yet to be carried out at any location and are not recommended as a GAW long-term routine measurement. However, periodic characterization studies of aerosol organic carbon speciation at suitable GAW stations are encouraged. Such studies will help identify the sources of organic carbon components. Collaboration of GAW network stations with those few laboratories having a demonstrated expertise is highly encouraged for these types of studies together with initiatives to better harmonize measurement protocols for specific organic tracer determination (i.e. levoglucosan) .

### **3.3.6 Location and distribution of analytical chemistry facilities**

A global atmospheric aerosol chemistry effort will involve collaboration between GAW and contributing partner networks. In order to merge the observations, laboratories must routinely participate in laboratory intercomparison programmes and integrate the comparison results when submitting data to WDCA. Implementation of a World Calibration Centre for Aerosol Chemistry would be highly supported by GAW. Although it is desirable to minimize the number of chemical laboratories within a network, there are also advantages in distributing the chemical analyses amongst enough laboratories within the network to minimize the time between sample collection and analysis. This is particularly true for mass and major aerosol ionic constituents. Furthermore, there are advantages in national capacity building. For multi-elemental and carbon-related analyses, where large analytical facilities and a great deal of expertise are required, respectively, it is recommended that the analyses be done at as few facilities as possible.

## **3.4 Sample handling protocol**

This chapter provides general guidelines for a sample handling protocol for filter based chemical aerosol measurements at GAW stations. Detailed protocols can be worked out by the national network. Filters should be loaded into filter holders (filterpacks) in a clean environment at a central facility to minimize the need for clean room facilities and associated training at each site. Contamination and filter loss are avoided by minimizing filter handling. The loaded filterpacks should then be shipped sealed to the stations. A significant number, between 5-10%, of all filters and filterpacks should be used as field blanks. Field blanks are treated exactly like a sample even to the point of mounting them in the sampling device. The

only difference is that air is not drawn through them. Sampling should be avoided during episodes of local pollution (see Chapter 2.4). Presumably, the site selection process of the GAW station will have minimized the impact of local pollution; nonetheless, criteria must still be developed to minimize the effects of local pollution on the measurements and instrumentation designed to implement the criteria. Field logs for each sampled filterpack must be maintained. The logs must record all relevant information related to the sampling of each filter pack, including a brief description of the meteorological conditions for the sampling period, and activities that may affect the sampling, and other QC flags. The exposed filterpacks should be resealed after sampling, stored in a dark location and returned to the laboratory as soon as possible to minimize the time between sampling and analysis. During shipping to the laboratory and during storage at the laboratory, samples should be kept cool to avoid volatilization and chemical changes. Field logs of critical sampling information should be copied and sent along with the filterpacks to the laboratory. Ideally, flow rate records should also accompany the filterpacks to the laboratory. In the laboratory, such information can be used in screening for proper sampling. Ideally, all of the record keeping at the field sampling stage will be conducted electronically with proper computer software designated for this purpose, and the records can be transmitted electronically to the laboratory in addition to the physical record handlings as described above.

Filterpacks should be unloaded in a clean environment, for example, in a filtered flow hood or glove box in which the air contains no particles, ammonia or other semi-volatile gases. The filterpacks need to be cleaned before new filters are loaded again.

### 3.5 Continuous instrumentation

Over the last decade, research and development efforts have been made to automate and combine the tasks of aerosol sample collection and analysis, and to develop continuous or semi-continuous instrumentation (Baltensperger et al., 2001). These efforts have achieved notable breakthroughs. Major advancements in measurement technologies have been made. New instruments are continuously being refined to the degree worthy of consideration for network deployment, and data extraction and reporting routines are maturing. Particularly noteworthy are the instruments for aerosol mass, chemical composition and black carbon mass measurements which are now provided by commercial companies. Deployment of these instruments increases the information available on chemical properties of aerosols, especially the time resolution, compared to the routine filterpack sampling and laboratory analysis as described above at the GAW network. For certain GAW activities, such as the IAGOS (In-service Aircraft for a Global Observing System) routine measurements from civil aviation aircraft, high time resolution is a pre-requisite for measurement; although the current crop of continuous instruments may not yet meet other technical requirements for such deployments.

Starting in the late 1990s, the TEOM (Tapered Element Oscillating Microbalance) has been widely used for aerosol mass measurements. The instrument provides continuous measurements and can produce high time resolution data. The original TEOM has a recommended temperature setting of 50°C. There is evidence that semi-volatile components of aerosols are lost from the TEOM measurements at this temperature. The most likely explanation is that semi-volatile organic compounds, nitrates, and water are lost from the aerosols during sampling. In newer TEOM models, the operating temperature has been lowered to 30°C to reduce losses of the semi-volatile components. In addition, sudden changes in ambient relative humidity may cause negative mass readings from the instrument. New modifications have been made to dry the aerosol particles before measurement to reduce the effect of ambient relative humidity (Baltensperger et al., 2001). However, biases due to volatility with aerosol sampling in the TEOMs have often been found to be relatively high despite the conditioned inlet. As a result, deployed TEOMs have started to be replaced by other instruments in some air quality monitoring network.

A competing type of continuous or semi-continuous aerosol mass measurement instrument is based on the principle of  $\beta$ -ray attenuation by aerosol mass. The  $\beta$ -ray source is usually  $^{14}\text{C}$  or  $^{85}\text{Kr}$  decay and the attenuation can be calibrated with a known mass. Sampling can be done

with individual filters or filter tapes, and the *b*-ray that passes through the filter is continually monitored. The *b*-meters may have the same inherent difficulties concerning volatilization as the TEOM depending on inlet configuration. However, comparison with gravimetric methods usually produces reasonable agreement (Baltensperger et al., 2001). Several companies offer *b*-meter instruments. Most *b*-meter instruments are based on semi-continuous methods, typically at 30 min or longer time resolution. One instrument gaining acceptance is the Thermo Scientific Synchronized Hybrid Ambient Real-time Particulate monitor (SHARP) 5030, which is built on the *b*-ray attenuation principle but at the same time combines aerosol scattering measurements to improve the accuracy of aerosol mass measurements. The SHARP 5030 can measure aerosol mass at 1 minute resolution, or longer depending on the aerosol load. This instrument is recommended as a Federal Equivalent Method (FEM EQPM-0609-184) for PM<sub>2.5</sub> measurements by the US Environmental Protection Agency (US EPA).

In terms of chemical components in aerosols, there have been significant technical advances leading to instruments for real time continuous measurements of aerosol black carbon mass, sulphate, nitrate, ammonium, and organic mass concentrations. For aerosol black carbon particles, the Single Particle Soot Photometer (SP2) instrument has been successfully used to measure particle refractory black carbon (rBC) mass and number concentration in air (Kondo et al., 2011). The SP2 instrument measures the intensity of incandescence light emitted from refractory black carbon mass in a single particle, ranging between 0.5 to 300 femtograms (fg), when it absorbs laser energy and is hence heated to approximately 4000°C. The rBC mass in the particle is proportional to the incandescence light intensity and thus can be quantified. Using the same measurement principle, High Resolution Laser Induced Incandescence (HSLII) instruments measure the integrated rBC mass of an ensemble of particles in a given air volume, including rBC masses smaller than 0.5 fg (down to an rBC mass with an equivalent ~5 nm particle diameter). SP-AMS instruments, which combine the SP2 laser light absorption module with an Aerosol Mass Spectrometer, allow measurements of rBC mass and its carbon clusters (Onasch et al., 2012). Time resolutions of SP2, HSLII, and SP-AMS measurements in ambient air can be very high, from sub-second to minutes.

The Aerosol Chemical Speciation Monitor (ACSM), a simplified version of aerosol mass spectrometer, is a continuous instrument that measures concentrations of aerosol sulphate, nitrate, ammonium, chloride, and organic mass at the same time. In an ACSM, particles in air are sampled into a differentially pumped high vacuum chamber, and are collimated using an aerosol lens in a trajectory that leads to aerosol impaction on a heater maintained at ~600°C (Ng et al., 2011). Upon contact with the heater, the non-refractory components of the particles are vaporized and ionized by electron impact, resulting in charged mass fragments which are detected either by a quadrupole or a time-of-flight mass spectrometer. Signals of the mass fragments are used to determine the concentrations of sulphate, nitrate, ammonium, chloride, and organic mass using ionization efficiency calibrations based on ammonium nitrate and the known (or assumed) relative ionization efficiencies for the other components. Time resolution can be as short as minutes depending on the aerosol loadings. The current sampling inlet design of the ACSM only allows the instrument to sample aerosols within the ~0.05-1.0µm (Ng et al., 2011).

Other recent technical developments have also allowed online aerosol chemical composition measurements. For example, aerosol particles can be collected onto impaction plates where sulphate and nitrate are converted into SO<sub>2</sub> and nitric oxides, respectively, for online detection. Stolzenburg and Hering (2000) recently demonstrated a system that samples aerosols by impacting them onto a metal plate, vaporizing the particles at high temperature, and converting nitrate into NO<sub>x</sub> for detection by chemiluminescence. The comparison with denuder-filterpack measurements of nitrate is reasonable. These instruments are typically for one species per instrument due to their detection methods, but can sample the larger aerosols >1µm diameter.

It should be noted that the continuous and semi-continuous instrumentations are not a panacea to the GAW aerosol chemical measurement programme. While there are obvious advantages of deploying these types of instruments in place of the regular filterpack sampling programme, there are also issues with using these instruments for long-term trend measurements. Firstly, the suitability of these continuous aerosol instruments for long-term deployment at GAW stations needs to be fully evaluated. While some Federal Equivalent Methods have been established for several aerosol mass measurement instruments by the US EPA, the other continuous instruments have only until now been undergoing evaluations. Deployment of SP2 instruments for black carbon measurements at a few GAW stations has started; assessment of the suitability of such SP2 deployment for long-term measurements will be shortly available. The ACSM has been deployed at a number of Global and Regional GAW Stations also on an evaluation basis. Several challenges have emerged from these deployments. Particular concerns include instrument stability and durability over long periods of deployment and uncharacterized collection efficiencies as a function of aerosol chemical composition. Initial developments to establish a calibration centre for online aerosol chemistry are highly encouraged by GAW.

Secondly, there needs to be applicable standard operating procedures, appropriate reference materials and established calibration routines when the continuous instruments are deployed across a network such as the GAW. Given the complex natures of these instruments, standard operating procedures need to be established for network deployment, a task to be completed. Instrument operation and calibration pose significant challenges especially for remote stations, and when there is a need for specialized accessory instruments for calibration. There will be a need for a centralized facility to conduct and coordinate periodic network instrument intercomparison for the continuous instruments as a quality assurance measure. An additional challenge is the large data volumes from these continuous instruments and their post measurement processing, which will require significant resources for QA/QC and analysis.

Thirdly, the costs for a comprehensive aerosol chemical composition monitoring programme using continuous/semi-continuous instruments are expected to be higher than the regular filterpack sampling/laboratory analysis. The choice of continuous instruments would mean that multiple continuous instruments will be needed at multiple sites; this may limit the number of sites and thus spatial coverage that can otherwise be maintained with the regular methodologies under a same funding envelop. The effort in quality assurance and quality control of the large volumes of continuous data and analysis will likely add more cost compared to the regular filter sampling and laboratory analysis.

Lastly but perhaps more importantly, there are technical limitations to the continuous instruments; for example, with the SP2 the rBC mass detection range is typically between 0.5-300 fg; the low end of the SP2 instruments may miss the portion of particles containing very small rBC masses. At the present time, this part is estimated through extrapolation of the rBC mass size distribution. The ACSM cannot provide information on refractory components of aerosols, and misses the chemical composition of super-micron particles. Hence for a comprehensive aerosol composition determination, many types of continuous/semi-continuous instruments would be needed to replace the regular filterpack sampling/laboratory analysis approach, negating some of the advantages of continuous instruments. An optimal approach may be a combination of the regular filterpack sampling/laboratory analysis methodology with some continuous instruments to obtain complementary observations.

If continuous instruments are to be used to replace the regular filterpack sampling/laboratory analysis recommended by GAW, an equivalence must be established between the two methods. To establish such equivalence, a rigorous approach needs to be followed that assesses the accuracy and precision of the continuous instruments, similar to that followed by the US EPA when establishing the FEMs.

### 3.6 Quality assurance and quality control plans

The goal of a GAW chemical aerosol measurement is for accurate long-term records, on a decadal or multi-decadal scale. Hence it is imperative that the measurement activities be quality assured and the data quality controlled, preferably by designated personnel. Here a general description of QA/QC principles is given as a basis from which the individual stations can modify or adopt as their guidelines for the long-term QA/QC plans. In addition to the field logs (physical or electronic), it is recommended that for GAW stations undertaking chemical measurements, a record of sample recovery rate for each network station should be maintained on a fixed schedule, such as monthly or quarterly. These records can be used as a basis for corrective actions if needed.

Compliance with the standard operating guidelines and procedures for sampling and analysis should be documented on the same schedule. For these matters, compliance criteria from the SOPs must be developed against which checks can be made. After completion of chemical analysis, QC checks must be performed on the raw data to flag questionable analyses that need repeat analyses. All analytical results must be properly combined with field data, such as air volume for each sample, to derive the final air concentration data. All such data must be recorded using well-documented formats on an electronic data system as described in chapter 9. Data that needs to be recorded include sampling data, sampling flags, calibration data, sample recovery rate survey, analytical results, lab flags, and compliance. These data must be combined with the ancillary measurement before they are recorded at the central data centre.

Analytical procedure quality control should consist of at least three steps: i) performance check by involving the lab in inter-laboratory intercomparisons; ii) distribution of QC standards with regular samples in a routine analysis sequence; iii) regularly scheduled repeat analysis of the same samples. Separate sets of flags must be developed for sampling/sample handling and analysis. The flags must be recorded with final results before submission to a central repository. Quality assurance includes regularly scheduled calibrations, as well as flagging of data with known problems for continuous and on-site measurements. It must be emphasized that proper standards must be used to calibrate these instruments. The raw data, along with the flags and the calibrations, must be properly archived. On a regularly scheduled basis, these data must be properly converted into final concentrations and be recorded using a predefined format for submission to a data centre. Data delivery to the GAW World Data Centre for Aerosols should be done on the same schedule as the sample recovery survey.

With emerging and increasing deployment of continuous instruments for aerosol chemical observations at GAW stations, it is important to consider the following quality assurance protocols or set goals to achieve them:

- 1) Establish equivalence with known reference methods such as the US EPA Federal Reference Methods using filter pack sampling and laboratory analysis.
- 2) Establish standard operating procedures for the continuous instruments. This can be based on manufacturer's recommendations or from other relevance sources, such as those that may be provided by the US EPA, but adopted for the GAW network.
- 3) Establish network centres for periodic instrument intercomparison, and provide expert advice on instrument operation for the cases where the GAW network is the pioneer for long-term deployment of some specific types of continuous instruments.
- 4) Establish standard procedures for data extraction, processing, and reporting.

As continuous instruments become mature and costs decrease, it is expected that they will become more widely deployed for long-term measurements at the GAW and other networks. Quality assurance and quality control protocols of the large data volumes from these instruments will need to be formulated and implemented before data submission to the WDCA begins.

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## CHAPTER 4. IN SITU MEASUREMENTS OF AEROSOL RADIATIVE PROPERTIES

### 4.1 Introduction

Knowledge of aerosol radiative properties is needed for the evaluation of effects of aerosol particles on climate and air quality (visibility). The fundamental quantity of interest for these applications is the aerosol particle cross-section for light extinction per unit volume of air, commonly called the (aerosol) particle light extinction coefficient ( $\sigma_{ep}$ ) and reported in units of  $\text{m}^2 \text{m}^{-3}$  (i.e.,  $\text{m}^{-1}$ ),  $\text{km}^{-1}$ , or  $\text{Mm}^{-1}$  ( $10^{-6} \text{m}^{-1}$ ). The particle light extinction coefficient is the sum of the particle light scattering ( $\sigma_{sp}$ ) and light absorption ( $\sigma_{ap}$ ) coefficients. Local visual range is related to the total ambient light extinction coefficient (at 550 nm wavelength) by the Koschmieder (1924) relationship,  $V = 3.9 / s_e$ , where light scattering and absorption by both particles and gases contribute to the total ambient light extinction coefficient, i.e.  $\sigma_e = \sigma_{ep} + \sigma_{eg}$ . Light scattering by gases ( $\sigma_{sg}$ ) is a well-known quantity that is directly proportional to air density and inversely proportional to the fourth power of wavelength, with a value of  $12.3 \text{Mm}^{-1}$  at standard temperature and pressure (273.15 K, 101.325 kPa), at 550 nm wavelength; see Bodhaine et al. (1999) for details. Absorption of solar radiation by gases is generally negligible compared to light scattering, except in plumes containing high concentrations of  $\text{NO}_2$ .

For radiative climate studies, information on the angular distribution of scattered light and the relative amounts of light scattering vs. absorption is required, in addition to the integral through the vertical column of the particle aerosol light extinction coefficient (aerosol optical depth, see Chapter 7). Combined interpretation of aerosol optical depth and surface-based measurements of particle light scattering and absorption coefficients requires knowledge of the vertical distribution of aerosol particles, which can be obtained from lidar measurements (see Chapter 8). Additional information on the mass scattering cross-section of major aerosol species, combined with knowledge of the dependence of aerosol particle radiative properties on relative humidity (RH), allows calculation of aerosol particle radiative effects from model predictions of spatial distributions of various aerosol species. Ogren (1995) and Heintzenberg and Charlson (1996) have presented overviews of the aerosol properties needed to determine the influence of particles on the Earth's radiative balance, and Table 4.1 gives a summary of these properties.

**Table 4.1. Aerosol particle radiative properties needed for climate studies**

$\sigma_{ep}$ , $\sigma_{sp}$ , $\sigma_{ap}$	The volumetric cross-section for light extinction is commonly called the <b>particle light extinction coefficient</b> , typically reported in units of $\text{Mm}^{-1}$ ( $10^{-6} \text{m}^{-1}$ ). It is the sum of the <b>particle light scattering and absorption coefficients</b> , $\sigma_{ep} = \sigma_{sp} + \sigma_{ap}$
$\delta$	<b>Aerosol optical depth</b> , defined as the integral over the vertical column of the aerosol light extinction coefficient.
$\omega_o$	The <b>aerosol particle single-scattering albedo</b> , defined as $\sigma_{sp}/\sigma_{ep}$ , describes the relative contributions of particle scattering and absorption to the particle light extinction. Purely scattering aerosol particles (e.g., sulphuric acid) have values of 1, while very strong absorbing aerosol particles (e.g., black carbon) have values of around 0.3.
$g, \beta$	Radiative transfer models commonly require one of two integral properties of the <b>angular distribution of scattered light</b> (phase function): the asymmetry factor $g$ or the upscatter fraction $\beta$ . The asymmetry factor is the cosine-weighted average of the phase function, ranging from a value of -1 for entirely backscattered light to +1 for entirely forward-scattered light. The upscatter fraction $\beta$ gives the fraction of sunlight scattered in the upwards direction (back to space), which depends on the solar zenith angle as well as the size distribution and chemical composition of the particles. $\beta$ can be estimated from hemispheric backscatter fraction $b$ (see chapter 4.2).

$MSC_i$	The <b>mass scattering cross-section (MSC)</b> , for species $i$ , often calculated as the slope of the linear multiple regression line relating $\sigma_{SP}$ and the mass concentration of the chemical species, is used in chemical transport models to evaluate the radiative effects of each chemical species prognosed by the model. This parameter has units of $m^2 g^{-1}$ .
$MAC_i$	The <b>mass absorption cross-section (MAC)</b> , for species $i$ , often calculated as the slope of the linear regression line relating $\sigma_{AP}$ and the mass concentration of the chemical species, is used in chemical transport models to evaluate the radiative effects of each chemical species prognosed by the model. This parameter has units of $m^2 g^{-1}$ .
$f(RH)$	The functional dependence of components of the aerosol light extinction coefficient ( $\sigma_{ep}$ , $\sigma_{sp}$ , $\sigma_{ap}$ ) on relative humidity, expressed as a multiple of the value at a low reference RH (typically <40%).

All of the above parameters are needed as a function of wavelength. The Ångström exponent for scattering,  $\beta_s$ , defined by the power-law  $\sigma_{SP} \propto \lambda^{-\beta_s}$ , describes this wavelength-dependence for scattered light. The literature on aerosol optical depth uses the symbol  $\alpha$  to denote the Ångström exponent.

Similar formulations are used to describe the wavelength dependence of aerosol optical depth and particle light absorption ( $\beta_a$ ). Situations where the light scattering and optical depth is dominated by submicrometer particles typically have  $\beta_s$  of approximately 2 (for the 550-700 nm wavelength pair), while values close to 0 occur when the scattering is dominated by larger particles such as mineral dust or sea salt. The absorption Ångström exponent is largely controlled by chemical composition and mixing state of the absorbing particles, rather than their particle number size distribution. Several wavelengths, spanning the visible spectrum, are recommended for GAW measurements. It would be desirable to harmonize these wavelengths with ones used by other spectral sensors to monitor the atmospheric aerosol (from surface-based or satellite-borne remote sensors), but there is a large number of wavelengths currently in use. Thus, comparison with other instruments will often require interpolation between whichever wavelengths are used. Many of the instruments for determining particle light scattering and absorption coefficients have a channel at about 550 nm, which is near the middle of the visible spectrum and provides a reference wavelength for comparing different sites and for comparison with standard visibility observations. Blanchet (1982) showed that values of  $\sigma_{ep}$ ,  $\omega_0$  and  $g$  measured at about 700 nm wavelength can be used in radiative transfer models to represent the values of these parameters averaged over the solar spectrum. Thus, 700 nm is a good choice as a second wavelength after 550 nm for use in climate studies. Finally, because of strong wavelength-dependence that some absorbing species (e.g. hematite contained in mineral dust, and some organic species) show at shorter wavelengths, a third wavelength at 450 nm or below is recommended.

## 4.2 Aerosol particle light scattering

Particle light scattering coefficient,  $\sigma_{sp}$ , is measured with an integrating nephelometer (see e.g. Heintzenberg and Charlson, 1996). Integrating nephelometers have been operated at baseline monitoring stations since the deployment of a four-wavelength instrument at NOAA's Mauna Loa Observatory in 1974. Presently, the GAW Station Information System (GAW SIS, <http://gaw.empa.ch/gawsis/default.asp>) reports that  $\sigma_{sp}$  is measured continuously at 21 Global GAW stations, 25 Regional GAW stations, and 29 Contributing stations around the globe. Some of these stations are operating single-wavelength units, but most are measuring  $\sigma_{sp}$  at three wavelengths. At present, there are two models of multi-wavelength integrating nephelometers in use at GAW stations: the TSI model 3563 (TSI, St. Paul, USA) and the Ecotech Aurora 3000 (Ecotech, Melbourne, Australia). These instruments operate at slightly different wavelengths in the blue, green, and red parts of the spectrum (TSI: 450, 550, and 700 nm; Ecotech: 450, 525, 635 nm) and have the added feature of being able to measure  $\sigma_{sp}$  over two angular ranges: total scattering (TSI: 7-170°; Ecotech: 9-170°) and hemispheric backscattering (90-170°, denoted as  $\sigma_{bsp}$ ). While instruments do not exist for direct determination of the asymmetry parameter,  $g$ , or upscatter fraction,  $\beta$ , the ratio  $b = \sigma_{bsp}/\sigma_{sp}$  can be used to estimate either of these parameters (Marshall et al., 1995; Wiscombe and Grams, 1976; Andrews et al., 2006). The Ecotech Aurora 4000 resembles the model 3000,

except that multiple angular integration ranges can be selected; this feature allows determination of the scattering phase function and calculation of the asymmetry parameter directly. The high sensitivity, multiple wavelengths, and backscatter capability of the TSI 3563 and Ecotech Aurora 3000/4000 make them most suitable for monitoring aerosol light scattering properties in support of radiative climate studies. Simpler, less expensive, less sensitive, one-wavelength instruments are also commercially available. These instruments can provide useful information on particle light scattering coefficient for air quality studies at urban or regional sites where elevated particle mass concentrations allow the use of a less sensitive instrument, and where the backscatter information is not required.

The procedures described below are mostly based on experience with operating the TSI 3563, but the general considerations apply to other nephelometers as well.

Anderson et al. (1996) reported the results of a comprehensive laboratory determination of the performance of the TSI 3563 integrating nephelometer, including characterization of its sensitivity, linearity, angular response, and wavelength response. They reported that instrument "non-idealities introduce uncertainties of less than 10% for typical accumulation mode particle sizes (i.e. volume mean diameters between 0.2 and 0.4  $\mu\text{m}$ )", but the errors in  $\sigma_{\text{sp}}$  for particles larger than 1  $\mu\text{m}$  diameter are 20-50%. Anderson and Ogren (1998) recommended several specific operating procedures for the TSI 3563:

- 1) The preferred calibration gases are air and  $\text{CO}_2$ .
- 2) Routine measurements of the calibration gases are desirable.
- 3) Supermicrometer particles should periodically be excluded from the sample stream. A cut size of 1  $\mu\text{m}$  (aerodynamic diameter at low RH) is recommended. Note, however, that this approach is not a strong recommendation for GAW stations.
- 4) For extinction budget studies, correction factors for the effects of angular non-idealities should be applied.

Subsequently, Heintzenberg et al. (2006) and Müller et al. (2011) reported the results of laboratory studies of the performance characteristics of nephelometers manufactured by Radiance Research and Ecotech, and compared the performance of these instruments with the TSI 3563.

Calibration is achieved by filling the instrument with a particle-free gas that has a known scattering coefficient. Most instruments use filtered, ambient air as the downscale calibration point, and  $\text{CO}_2$  as the upscale point. Generally, calibrations with air are performed automatically once per hour to once per day. It should be made clear that the schedule for air calibrations controls the precision of the determination of the instrument background, which is subtracted from the measurements to obtain the particle light scattering coefficient; any error here gravely affects the detection limit of the instrument. For this reason, the frequency of air calibrations should be chosen so that the zero drift between calibrations is much less than the minimum particle light scattering coefficient at the site. At least one air calibration per day should be performed. Evaluation of hourly air calibrations of TSI 3563 nephelometers at 20 GAW stations (a total of 0.5 million measurements) yielded a precision (95% confidence) of the instrument background determinations of  $\pm 0.32$ ,  $\pm 0.17$ , and  $\pm 0.26 \text{ Mm}^{-1}$  for the blue, green, and red wavelength channels, respectively.

Calibrations with other gases should be performed much less frequently (every 2-12 months). Tests by NOAA with weekly measurements on  $\text{CO}_2$ , for 18 different TSI 3563 nephelometers at 14 stations (3823 total measurements) indicate that the precision of nephelometer calibrations (95% confidence) is 3.3%, 3.5%, and 5.2% for the blue, green, and red wavelength channels, respectively.

$\sigma_{\text{sp}}$  shows a strong dependence on relative humidity, and interpretation of integrating nephelometer data requires knowledge of the RH in the sample volume. This RH can be lower than the RH at the inlet due to heating of the air by the light source in nephelometers that use

incandescent lamps. For the TSI 3563, this heating is typically 4-5°C, but it can be reduced to about 1°C by operating the instrument with the covers removed and using an external fan to increase ventilation around the lamp; in contrast, the LED light source in the Ecotech Aurora 3000/4000 does not appreciably heat the sample air. Fortunately, the RH-dependence below about 40% is fairly weak, so a precise determination of RH is not required if it is kept below this level. Comparison of results from different locations is facilitated by choosing a reference humidity for operating the instrument. The inlet system used at a GAW aerosol sampling site should include RH-control, obviating the need for a separate RH-controller for the nephelometer. However, the recommended sampling protocol includes measurement of RH inside the nephelometer, and we recommend a value of 30-40% for the reference relative humidity.

Measurements of  $f(RH)$  require a second nephelometer, directly downstream of a humidifier. Anderson and Ogren (1998) reported minimal particle losses in the TSI 3563 nephelometer, making it appropriate to operate the humidified nephelometer downstream of a nephelometer operated at a low, reference RH; the humidified nephelometer could also be operated in parallel with the reference nephelometer. The expense and complexity of this measurement preclude its implementation at most GAW sites, but it is desirable to obtain these measurements at a range of sites that covers a variety of aerosol types (Zieger et al., 2013).

Aerosol particle filter samples should be collected in two size fractions (see Chapter 3). One of the possible derived products from the GAW integrating nephelometer sampling is the mass scattering (and backscattering) cross-section for the chemical species determined from the filter samples. To accomplish this, the aerosol supplied to the integrating nephelometer should be size-segregated, with the same size cuts as used for the filter samples. This can be achieved by placing an impactor, in parallel with a ball valve, in the air stream ahead of the nephelometer. By automatically opening and closing the ball valve every few minutes, values of the total (<10  $\mu\text{m}$  diameter) and submicrometer particle light scattering coefficient can be determined. However, the success of this approach requires a nephelometer with internal pressure and temperature sensors to automatically compensate for changes in sample air density induced by the impactor. Because of this complexity, size-resolved measurements of the aerosol particle light scattering coefficient are not a strong recommendation for GAW stations.

Routine maintenance for integrating nephelometers is minimal. The lamp and zero air filters are the only consumables in the instrument, and are easily replaced. Insects, spiders, and even birds have found their way inside nephelometers, but their effects are readily detectable in the data. With time, dust accumulation on interior surfaces can result in unacceptably high background levels, necessitating disassembly and cleaning. The key to identifying the need for maintenance is to maintain daily logs of diagnostic parameters (lamp current and voltage, internal reference brightness, power supply voltages, air calibration results), and to train the site attendants to look for gradual degradation or sudden changes in those parameters.

Modern integrating nephelometers are equipped with pressure and temperature sensors to allow compensation for changes in the scattering coefficient of air due to density changes. Internal relative humidity sensors are also available. The calibration of these sensors should be checked on an annual basis.

### **4.3 Aerosol particle light absorption**

There are two approaches currently in use for measuring particle light absorption coefficient, filter-based particle light absorption photometers (FAP) and photoacoustic spectrometers (PAS); see Moosmüller et al. (2009) for an overview of techniques. FAP instruments measure the rate of change of light transmittance and/or reflectance through a fiber filter as particles are deposited on it. The interpretation of observations requires compensation of the interaction between deposited particles and the filter matrix, either by applying correction schemes or radiative transfer codes. Furthermore, FAP methods for measuring the particle light absorption coefficient have been shown to be biased high under certain circumstances (Cappa et al.,

2008; Lack et al., 2008). However, FAP methods are very sensitive, less expensive, and simpler to operate than other methods. PAS instruments (e.g. Moosmüller et al., 1998; Arnott et al., 2003) illuminate the particles in a volume of air with a modulated laser beam, which heats the particles and consequently the surrounding air, and causes the pressure in the sample volume to change at the modulation frequency; this pressure change is detected with a microphone. These instruments measure the light absorption coefficient of the particles while they are suspended in air, which avoids the problems that result from interactions between the particles and the filter in FAP instruments.

The strengths and weaknesses of the two methods mean that PAS instruments are well-suited for calibrating FAP instruments, intensive field campaigns, and measurements in polluted regions, while FAP instruments are better suited for measurements at GAW stations in rural and remote regions.

Measurements of the particle light absorption coefficient are often reported as "black carbon", an interpretation of the data that has multiple weaknesses. Recognizing this problem, Petzold et al. (2013a) suggested terminology that uses "black carbon" as a qualitative descriptor of the substance and "equivalent black carbon" as the mass concentration of black carbon that would yield the measured light absorption. This terminology is recommended for reporting GAW measurements. A detailed discussion of MAC and MSC values of light-absorbing carbonaceous material is provided by Bond and Bergstrom (2006) and Bond et al. (2013).

Calibration of filter-based methods is difficult, but is required because the relationship between change in light transmission and particle absorption optical depth on the filter depends on many factors, including the particular filter medium and the light-scattering nature of the particles. Heintzenberg et al. (1997) discuss the methods used to determine  $s_{ap}$ , and conclude "there is a clear-cut need for standardization and intercalibration of measurements of light absorption coefficient." A dedicated workshop on black carbon reference materials for instrument calibration and intercomparisons (Baumgardner et al., 2012) stated that suitable standard reference materials are available for calibrating some, but not all, measurement methods. The workshop report still concludes that there are no procedures commonly agreed on to calibrate filter-based instruments that use the measurement of light attenuation to derive the particle light absorption coefficient.

Bond et al. (1999) and Weingartner et al. (2003) reported the first approaches for a calibration by means of comparison with reference techniques for laboratory test aerosols. The reported procedures require simultaneous nephelometer measurements to correct for substantial effects of light scattering by the particles on the filter. An in-depth intercomparison of absorption measurement methods is given by Sheridan et al., 2005. They report that, for atmospherically relevant levels of the particle light absorption coefficient, all participating PAS and FAP techniques agree within 11%, when correction schemes are properly applied. During subsequent absorption intercomparison workshops (Müller et al. 2011), a large spread of unit-to-unit variability of FAP instruments was found, ranging from 5% to 30% depending on instrument details. The observed unit-to-unit variability reinforces the need for careful calibration of flows and filter sampling spot sizes for individual units prior to deployment.

One FAP instrument in common use is the aethalometer (Magee Scientific, Berkeley, USA). Originally, this instrument was calibrated in terms of an equivalent mass of black carbon rather than the fundamental property that provides the instrumental response: aerosol light absorption. Interpretation of aethalometer data in terms of black carbon requires a value for the MAC of the black carbon particles. When deposited on the filter, a value of  $19 \text{ m}^2 \text{ g}^{-1}$  is commonly used for a wavelength of 880 nm; note, however, that this MAC value includes the interaction between the particles and filter, and is greater than the MAC value of black carbon particles suspended in air. MAC values ranging from 5 to  $20 \text{ m}^2 \text{ g}^{-1}$  have been reported for aerosols from different regions and different composition (Lioussé et al., 1993; Petzold et al., 1997), which implies that the MAC value must be determined experimentally at every site where FAP instruments are used to estimate black carbon mass concentrations (see Section 3.3.5.4).

Following recommendations by Petzold et al. (2013), aethalometer measurements should be reported primarily as the particle light absorption coefficient, and secondarily as the equivalent black carbon mass concentration. At present, there is no worldwide consensus about the most representative correction scheme that should be applied to aethalometer measurements, and experiments have indicated that the parameters of the correction schemes vary in time and space (Weingartner et al., 2003; Arnott et al., 2005; Collaud Coen et al., 2010; Drinovec et al., 2015). In the current absence of a consensus on aethalometer corrections, GAW stations are encouraged to submit uncorrected (Level 0, see Section 9.3) aethalometer data to the World Data Center for Aerosols, so that consistent results from all GAW stations operating aethalometers can be achieved once a consensus correction method becomes available.

The WCCAP has been actively involved in development of a correction method for model AE-31 aethalometers, using particle light absorption coefficients derived from simultaneous measurements with Multi-Angle Absorption Photometers (MAAP, see below) at several observatories with different aerosol types. The correction method endorsed by WCCAP, which was developed by the ACTRIS community uses a single multiplier ( $C_0$ ) to convert the measured attenuation coefficient ( $b_{ATN}$ ) to the particle light absorption coefficient ( $\sigma_{sp}$ ),

$$\sigma_{sp} = b_{ATN}/C_0$$

where the attenuation coefficient is calculated from the measurements reported by the AE-31 aethalometer as follows:

$$ATN = -100 \times \log_e \left( \frac{I}{I_0} \right)$$

$$b_{ATN} = \frac{1}{100} \frac{A \Delta ATN}{Q \Delta t}$$

In the above equations,  $I$  is the intensity of light transmitted through the sample filter,  $I_0$  is the intensity of light transmitted through the filter before sampling started,  $A$  is the filter spot area,  $Q$  is the flowrate, and  $\Delta ATN$  is the change in  $ATN$  measured over the time period  $\Delta t$ . The equivalent black carbon mass concentration reported by the AE-31 is related to the attenuation coefficient by

$$[EBC] = \frac{b_{ATN}}{SIGMA}$$

where  $SIGMA$  is the "Specific Attenuation" ( $22.2 \text{ m}^2 \text{ g}^{-1}$  at a wavelength of 660 nm) used by the AE-31. (Note that  $SIGMA$  is not the same quantity as the mass absorption cross-section described in Table 4.1, despite having the same units.)

A manuscript is in preparation that describes the new AE-31 correction scheme, and GAW is likely to adopt that scheme following its publication in a peer-reviewed journal. GAW stations that desire to submit corrected Level 1 and Level 2 aethalometer data to WDCA (see Section 9.3) should first submit the Level 0 data, and then use the above equations with  $C_0=3.5$  to calculate the particle light absorption coefficient. This value of  $C_0$  is the average of all the investigated datasets, and has an uncertainty of approximately 25%. Measurements done at the WCCAP indicate that the value of  $C_0$  holds for wavelengths between 450 and 700 nm. Data providers are advised to consult the latest online version of this document (<http://www.wmo-gaw-wcc-aerosol-physics.org/wmo-gaw-reports.html>) for possible updates to the correction scheme prior to submission of aethalometer data to WDCA.

Early models of the aethalometer have a very broad wavelength response, while newer versions offer narrow-band measurements at multiple wavelengths. Correction schemes have only been derived for instruments making narrow band absorption measurements, therefore it is recommended that broadband instruments not be used to measure the particle light absorption coefficient in the GAW network.



For the model AE33, similar studies as for the AE31 are in progress. Data providers are advised to consult the latest online version of this document (<http://www.wmo-gaw-wcc-aerosol-physics.org/wmo-gaw-reports.html>)

Bond et al. (1999) characterized the response of the Particle/Soot Absorption Photometer (Model PSAP, Radiance Research, Seattle, USA) to laboratory aerosols with different single-scattering albedos, using a calibration standard based on the difference between  $\sigma_{sp}$ , measured with a long-path extinction cell, and  $\sigma_{sp}$ , measured with an integrating nephelometer. They reported systematic errors in the manufacturer's calibration curve for the PSAP, as well as a response from non-absorbing particles. The correction scheme reported by Bond et al. (1999) should be applied to all PSAP results from GAW stations. The original, one-wavelength PSAP operates at a wavelength of 565 nm, but the calibration reported by Bond et al. (1999) is for a wavelength of 550 nm. The newer, three wavelength instruments operate at wavelengths of 467, 530, and 660 nm. These instruments, as well as one wavelength PSAPs operating at 530 nm, should use the modified form of the Bond et al. (1999) correction scheme reported by Ogren (2010). Other variants of the Radiance PSAP are being used at GAW stations, including non-commercial instruments manufactured by Stockholm University and NOAA, as well as a commercial version of the NOAA instrument (Tri-color Absorption Photometer, "TAP", Brechtel Manufacturing, Hayward, CA, USA).

Yet another filter-based instrument is the MAAP, produced by Thermo ESM Andersen Instruments (Erlangen, Germany). The MAAP uses a different optical configuration than the aethalometer and PSAP, with measurements of the filter reflectivity at two different angles in addition to the filter transmission measurement (Petzold et al., 2004). The two reflectivity measurements allow correction for multiple scattering processes involving the deposited particles and the filter matrix. This approach eliminates the need for a correction scheme based on independent measurements of aerosol light scattering coefficient (Petzold et al., 2005). The MAAP nominally operates at a wavelength of 670 nm, but laboratory tests revealed that the actual wavelength is 637 nm; as a consequence, particle light absorption coefficients and equivalent black carbon mass concentrations from the MAAP should be multiplied by a factor of 1.05 (Müller et al., 2011).

One way to reduce the contributions of scattering particles to absorption derived from FAP instruments is to heat the sample to ca. 300°C, which drives off most scattering particles from the filter and leaves only refractory particles behind (black carbon, mineral dust, sea salt). This approach is used by COSMOS (Kanonmax, Inc., Japan), and has been shown to yield results that are highly correlated with refractory black carbon and elemental carbon measurements (Kondo et al., 2011). Nevertheless, the primary measurement by this approach is particle light absorption, and the results should be reported first as absorption and secondarily as equivalent black carbon.

The particle light absorption measurements should use the same inlet system (humidity- and size-controlled) as the rest of the aerosol sampling system. The filter-based methods yield erratic results when the humidity changes, particularly at high relative humidity (Arnott et al., 2003). The guidelines given in Section 2.4 should be followed to ensure that the sample RH is kept below 40% in air-conditioned laboratories. Routine maintenance needs of the filter-based methods are minimal: i) change the filter when the amount of transmitted light gets too low (ca. 70% of the initial intensity) - the MAAP, COSMOS, and some aethalometer models perform this filter change automatically; ii) check the flowrate and lamp brightness regularly; iii) measure the sample area of the filter deposit (considerable unit-to-unit variation has been observed for the PSAP).

The PAS technique works well for urban environments (Arnott et al., 2005; Langridge et al., 2013). However, in clean regions the noise level of the instrument can be greater than the ambient signal, hindering accurate measurements of particle light absorption coefficient. The PAS uses an acoustic technique and any changing ambient noise (e.g. pumps) can affect the measurement. As a result, this instrument can have a drifting baseline especially when a zero

is performed. It is recommended to dampen the noise by attaching a coiled teflon tubing/muffler to the outlet. In very clean environments, it is also important to determine frequent zeros, at least once every hour, especially when the absorption measurements are close to the detection limit of the instrument. The inlet RH should be kept below 50% to avoid artifacts due to changing RH. The instrument must be calibrated properly.

#### 4.4 Aerosol particle light extinction

Although the particle light extinction coefficient is not on the list of recommended in situ aerosol measurements at GAW stations, it is of considerable value to GAW for two primary reasons. The first is to enable a comparison of measured extinction with the calculated sum of measured scattering plus absorption. If all the instruments are functioning ideally, the two measured and calculated values of extinction should be equal. If their difference is greater than the combined uncertainty of the measurements, then the calibrations and operating procedures of the three instruments need to be checked. Since FAP methods for measuring light absorption may be biased high by condensed organic compounds (Cappa et al., 2008; Lack et al., 2008), the independent measurement of particle light extinction allows assessment of a possible high bias in the particle light absorption coefficient.

The other application for measurements of the particle light extinction coefficient in GAW is as a component of a reference method for light absorption coefficient. The WCCAP uses the difference between particle light extinction and light scattering coefficients as a reference measurement of particle light absorption coefficient. Although the difference method is generally not suitable for measurements of particle light absorption in ambient air, where the uncertainty of the difference can be as large as the difference itself, this limitation is not as severe for controlled laboratory measurements of test aerosols.

Today, only one instrument, the CAPS PMex monitor (Cavity Attenuated Phase Shift, Particulate Matter extinction; Aerodyne Research, Inc., Billerica, MA, USA), is known to be in use at GAW stations and at WCCAP. The instrument's basic working principles are similar to cavity ring-down techniques (Massoli et al., 2010) and the instrument is available for several wavelengths in the visible spectrum. The instrument was found to agree with reference techniques and primary particle standards within less than 5% deviation and the unit-to-unit variability was below 4% (Petzold et al., 2013b). For ambient particle light extinction measurements, it is recommended to operate an instrument at a wavelength of 630 nm. If an instrument operating in the green spectral range is used, cross-sensitivities to NO<sub>2</sub> have to be considered.

Based on manufacturer's information, the CAPS PMex is calibration-free. However, routine checks of instrument performance by using CO<sub>2</sub> as a span gas is recommended; see calibration procedures for an integrating nephelometer for details. The CO<sub>2</sub> extinction cross-section for the given operation wavelength can be calculated according to Bodhaine et al., (1999). During long-term operation the reflectivity of the mirrors of the cavity may degrade, resulting in an increase of the total loss of the instrument (reported in Mm<sup>-1</sup>). Cleaning of the instrument mirrors is recommended when the total loss exceeds approx. 500 Mm<sup>-1</sup> at 630 nm.

General operating considerations for this instrument are the same as for other aerosol instruments: RH must be measured and should be maintained below 40%, and particle size control should match the other aerosol optical instruments.

#### 4.5 Data reporting, sampling frequency, data editing

The time resolution of the records of aerosol particle optical variables should allow generation of hourly statistics, preferably from integrals taken over 1 minute periods. Following the GAW data submission guidelines (Chapter 9), these should include arithmetic mean, as well as the 15.87 and 84.13 percentile values for each hour. Quality control of data is the responsibility of each observing station, and data known to be contaminated or otherwise corrupted should be

flagged. All measurements of aerosol optical properties should be adjusted to standard temperature and pressure (273.15 K, 1013.25 hPa).

#### 4.6 Quality assurance and quality control considerations (QA/QC)

Suitable aerosol standards do not exist for field audits of the performance of instruments for determining aerosol light scattering and absorption coefficients. Calibration of integrating nephelometers should be checked on a monthly basis by measuring the response of the instrument when filled with a gas whose scattering coefficient is known (carbon dioxide is an appropriate choice). A corresponding method for auditing the calibration of filter-based light absorption instruments does not exist, although highly desirable. Instead, it is recommended that GAW stations operating continuous light absorption photometers should periodically operate a travelling laboratory reference instrument, calibrated by an appropriate method, alongside the first for at least one week to check for long-term drift in instrument response.

Calibration of internal sensors for measuring flow rate, temperature, pressure, and relative humidity should be performed on an annual basis, and archived.

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## CHAPTER 5. PARTICLE NUMBER CONCENTRATION AND SIZE DISTRIBUTION

### 5.1 Particle number concentration

The particle number concentration represents a single integral measurement of particle number across a wide particle size range, encompassing basically the nucleation, Aitken and accumulation modes in the particle number size distribution. Such integral particle measurements serve various purposes:

- **Atmospheric trends:** The particle number concentration gives an indication of the instantaneous balance between particle formation and emission, and particle removal in the atmosphere.
- **Validation of particle number size distributions:** The particle number concentration is a useful adjunct to the determination of number size distributions. One tool to validate particle number size distribution methods is to compare the integral over the measured size range (here: mobility particle size spectrometer covering the ultrafine and fine size range) with the directly measured particle number size distribution.
- **Exposure of ultrafine and fine particles:** The particle number concentration of ultrafine particles (particles smaller than 100 nm) is also considered a possible factor in the adverse impact of atmospheric aerosol particles on human health (Oberdörster et al., 1995). In urban and rural environments, ultrafine particles generally comprise the major fraction of the particle number concentration.
- **Identification of local contamination episodes:** nearby combustion sources can cause high aerosol concentrations that should be flagged as local contamination. High particle number concentrations can be used to confirm cases of local contamination that cause elevated readings in other measurements at the station (e.g. particle light absorption coefficient), but it should be noted that high particle number concentrations can also be caused by new particle formation events.

#### 5.1.1 Condensation particle counter

The particle number concentration can be determined by condensation particle counters (CPC), which are commercially available. Modern CPCs are based on a continuous aerosol flow and work in a single counting mode. The working fluid most often used is butanol. The working principle of modern butanol CPCs can be simply described.

- The aerosol flow is saturated with butanol in a temperature-controlled saturator (e.g. 39°C in a TSI-CPC model 3772).
- In a cooling section (condenser), the temperature is decreased by 22 to 10°C, depending on the type of the CPC (e.g. TSI-CPC model 3772 vs. 3776), to achieve a nominal target 50% detection efficiency diameter (10 nm or 3 nm).
- The cooling causes a supersaturation of the aerosol with butanol vapour depending on the temperature difference between saturator and condenser.
- The butanol vapour condenses onto the particles and forms droplets of approximately 10 µm.
- The flow is then focused through a nozzle into an optical configuration (laser diode and photo detector), and each droplet is individually counted.
- The particle number concentration can be calculated, knowing the count rate and volumetric flow rate.
- Coincidence occurs when two droplets are in the detection volume at the same time. This is automatically corrected by the instrument or can be done afterwards. For a CPC such as the TSI model 3772, the coincidence error is about 3% for a particle number concentration of 10,000 cm<sup>-3</sup>. For this CPC, the internal correction allows particle number concentration measurements, e.g. up to 50,000 cm<sup>-3</sup>.

In order to ensure long-term quality-assured data, the CPC should be technically checked regularly and preferably calibrated against a reference standard every year. Experience suggests that the performance of CPC degrades typically after one year of continuous ambient measurements due to laser power deterioration or contamination of the focusing nozzle, critical orifice or the optics. When calibrating a CPC, particle losses inside the CPCs are implicitly included in the measured counting efficiency. Ideally, the CPC is compared at the calibration facility of the observational network or at the manufacturer. An accurate determination of the detection efficiency curve of a CPC depends strongly on the traceability of the reference instrument such as a calibrated aerosol electrometer, which measures the electric current of charged particles in an aerosol flow. From the electric current measured by an electrometer, the particle number concentration can be directly calculated by knowing the exact aerosol flow rate and assuming only singly charged particles.

### **5.1.2 Calibration**

In the following, the determination of the counting efficiency of CPCs is described as presently done at the GAW-WCCAP in Leipzig (Wiedensohler et al., 1997; Wiedensohler et al., 2012).

- A silver aerosol is nucleated after a tube furnace and monodisperse particles are selected in the range from 3–40 nm using a differential mobility analyser (DMA). For the size range up to 40 nm, mainly singly charged particles are achieved after the DMA. Due to the relatively small degree of polydispersity of the aerosol from the furnace generator (geometric standard deviation of 1.3–1.4), the concentration of double charged particles up to 40 nm is negligible.
- After dilution, the response of each CPC is then compared against a reference electrometer as a function of particle diameter. All CPCs and the aerosol electrometer are connected to a common manifold that is designed to minimize particle losses.
- In the first calibration step, several condensation particle counters such as TSI-CPC-3772 are used to compare the particle number concentration for 40 nm particles. Taking into account the actual flow rate of each particle counter, the unit-to-unit variability is normally maximum  $\pm 3\%$  at 40 nm around the mean value, if the counters are operating properly.
- At the WCCAP, a calibrated electrometer is used. It is regularly calibrated to a femto-Ampere source at the German national metrology institute (PTB).
- In case, all candidate CPCs and the reference CPC have a plateau counting efficiency of 100  $\pm 3\%$ , also the efficiencies for other particle size down to few Nanometers can be determined.

### **5.1.3 Network measurement**

A 50% detection efficiency diameter of 10 nm is recommended for CPCs for particle number concentration measurements within the GAW network. See also Wiedensohler et al. (1997) for examples of counting efficiency curves of various CPCs. Certain projects may have a wider scientific scope, which encourage to use an additional CPC with a lower 50% efficiency diameter of 3 nm (ultrafine CPC or UCPC). The difference of these two measurements is a measure of particle formation by homogeneous nucleation. In locations with large particle number concentrations such as urban or polluted areas, the selection of CPCs may need to include a model with upper concentration capacity in excess of  $10^5 \text{ cm}^{-3}$  (or a dilution of the sample flow). Since the major fraction of the particle number concentration is often in the ultrafine particle size range, the sample configuration should be optimized to minimize particle losses due to diffusion as described in Chapter 2.

- The length of the sample tube should be kept as short as possible
- The flow regime should be laminar
- The ideal flow Reynolds number is 2000
- The sample flow should be dried, but keeping the losses in the dryer minimal.



The time resolution of the measurements of particle number concentrations should allow for the understanding of fast processes in the atmosphere, preferably from 1 minute integrals. The exact data submission protocol for these measurements is available at the WDCA.

## **5.2 Particle number size distribution**

Measurement of the particle number size distribution can serve several purposes. At the broadest level, this can be used to infer relative contributions to the aerosol from different sources, such as the presence of strong coarse modes due to mechanical generation processes, or ultrafine modes due to new particle production from condensation processes. This information is useful in interpretation of the aerosol system in the sampled air mass. For a given location, long-term measurements are desirable. They can be used to identify aerosol sources especially when combined with aerosol chemistry observations. Measurements of particle number size distribution (PNSD) are also needed to test or validate regional chemical transport models, which include the PNSD. Other applications of the particle number size distribution include:

- Reconciliation of observed cloud condensation nuclei (CCN) through modelling based on observed particle number size distribution
- Explaining the observed particle mass concentration or the observed particle light scattering coefficient in a given size range in closure studies.

Because of the complexity of PNSD measurement, it is recommended that number size distribution determinations are undertaken only at GAW stations with more highly-developed aerosol programmes. There are several methods to determine the PNSD.

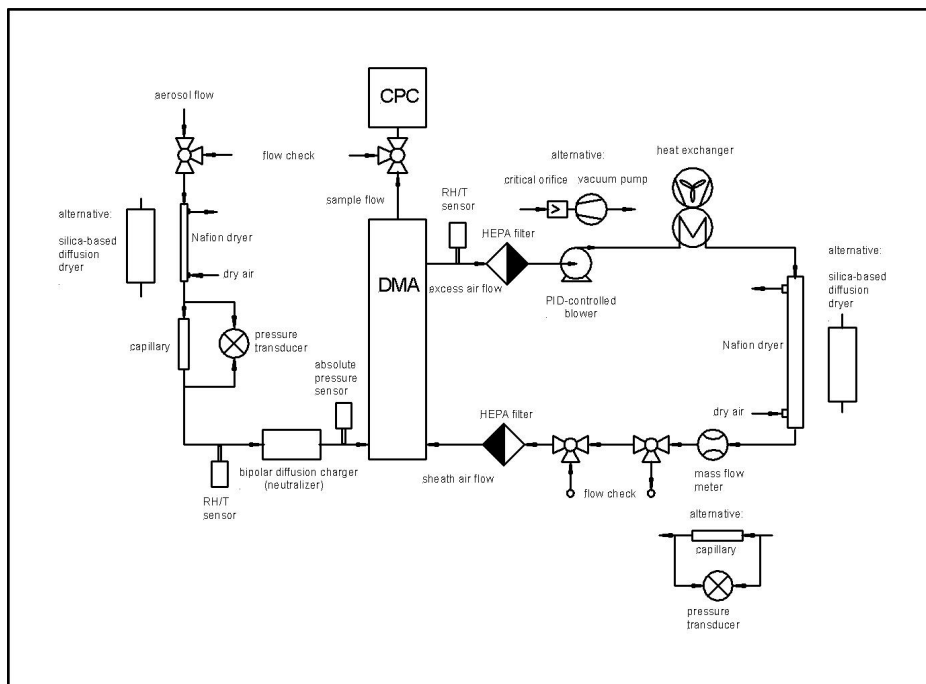
- Mobility particle size spectrometer based on the electrical particle mobility (3-800 nm, mobility diameter)
- Optical particle size spectrometer based on the intensity of particle light scattering (300 nm to few micrometres, optical diameter)
- Aerodynamic particle size spectrometer based on time-of-flight in an accelerated flow (700 nm to 10  $\mu\text{m}$ , aerodynamic diameter).

There are instruments commercially available for all methods, but also custom-built mobility particle size spectrometers. Only for mobility particle size spectrometer covering the ultrafine and fine particle size ranges have quality assurance protocols for atmospheric measurements been developed. In the context of the European Network ACTRIS, recommendations have been given in Wiedensohler et al. (2012). In the following, the emphasis is thus given to measurements using mobility particle size spectrometers, which are more commonly used in atmospheric observational networks than other methods for measuring PNSD.

### **5.2.1 Mobility particle size spectrometer**

#### *5.2.1.1 Recommended instrument set-up*

Parts of these standards have resulted from the desire to harmonize aspects of hardware, and enhance the accuracy and definition of the measurement. Others were conceived to enhance the data formatting and evaluation procedure of the measurements. The recommended standards have been clearly motivated by the needs of long-term field experiments, nurtured by a multi-annual practice of field observations and laboratory intercomparisons of mobility particle size spectrometers. The general spirit of these recommendations is to improve the accuracy and worldwide comparability of such measurements. We encourage operators of atmospheric measurements of particle number size distributions to adhere to these standards as far as possible and to upgrade commercial instruments accordingly. One important recommendation is that only instruments based on bipolar charging should be employed, because unipolar charging leads to increased uncertainties.



**Figure 5.1. Recommended set-up of a mobility particle size spectrometer for long-term measurements of the ambient aerosol (Wiedensohler et al., 2012)**

The schematic of the recommended mobility particle size spectrometer is shown in Figure 5.1. Here, the sheath air flow is circulated in a closed loop, a principle implemented in most commercial and custom-made mobility particle size spectrometers. The recommended set-up includes dryers to reduce RH in the aerosol sample and sheath air flows. The dryer in the sheath air flow helps to avoid measurements with moist air somewhere in the DMA and to achieve a stable relative humidity in the system. Furthermore, it reduces the time lag to dry all flows and HEPA (High Efficiency Particle) filters. The sheath air loop contains a heat exchanger and HEPA filters. Sensors continuously record the aerosol and sheath air flow rates, relative humidity and temperature in both flows, and absolute pressure in the aerosol flow entering the DMA.

For “scanning” mobility particle size spectrometers, a minimum scanning time (up or down scan) of two minutes is recommended to avoid smearing effects in the particle counters with a relatively slow response time. These smearing effects can cause, for example, significant false measurements at the slope towards larger particles in the accumulation mode range.

### Relative humidity control and measurement

Due to the hygroscopic growth of atmospheric aerosol particles at RH well below supersaturation, it is essential to control or limit RH in mobility particle size spectrometers. The philosophy is to obtain comparable datasets and, therefore, to measure the “dry” particle number size distribution. When working in a warm and moist atmospheric environment, the dew point temperature can reach the standard temperature of a measurement laboratory (20-25°C). This requires that the aerosol sample flow has to be dried, either directly in the main sampling line or at the instrument. A dry aerosol sample is needed to ensure the correct bipolar charge equilibrium and, thus, sizing downstream of the bipolar diffusion charger in the DMA. A dry sheath air is needed to ensure particle sizing inside the DMA with a minimum fluctuation in RH. The recommendation is to limit RH inside an instrument to below 40%. In this regime, changes in particle diameter as a result of RH are expected to be below 5%. To limit RH in the aerosol sample flow (see also the recommendation for the drying), we concretely recommend using a membrane dryer (made from materials such as Nafion™), or a silica-based aerosol diffusion dryer. Operation of a membrane dryer will require a continuous supply of dry air in the laboratory, while a silica-based dryer will require regular

regeneration. Utmost care should be taken to select or design dryers that feature minimum particle losses, such as due to Brownian diffusion. Ideally, particle losses across the dryer are characterized and accounted for in the data processing as an equivalent pipe length (see Section 5.2.1.2).

In complete analogy, the sheath air flow rate should be dried below 40% RH as well. Both membrane and diffusion dryers can be used. RH in the sheath air flow should be monitored continuously by a calibrated humidity sensor as well. The sheath air RH sensor should be installed as close as possible to the DMA at the excess air outlet. The objective is to measure RH at a temperature and pressure that best represent the conditions inside the DMA. As a guideline, the temperature of the sheath air RH sensor should not differ more than 1 K from the temperature in the DMA if possible.

RH in both the aerosol and sheath air flows should be monitored continuously by calibrated humidity sensors with a maximum uncertainty of maximum 5% RH across the range of 10-90%. These data should be recorded and stored with at least the same time resolution as the electrical particle mobility distributions. When dual mobility particle size spectrometers (systems with two parallel DMAs) such as a TSMPS (Twin Scanning Mobility Particle Sizer) are used to cover a wider particle size range (e.g. below 10 nm), the RH parameters should be separately reported for each DMA.

### **Sheath air and aerosol flow specifications**

In the case of a closed-loop sheath air flow, a heat exchanger is needed to remove the excess heat generated by the pump or blower. An ideal instrument employs two HEPA filters to provide particle-free sheath air at the exit from and entrance to the DMA. The pressure drop across the HEPA filters should be minimal to ensure a correct measurement in the closed loop of the sheath air flow. For a critical orifice/pump set-up, the absolute pressure downstream of the critical orifice should be monitored to ensure critical flow conditions (pressure downstream less than half of the upstream pressure).

One of the important but sometimes apparently underestimated issues in particle electrical mobility measurements is the correct determination of the instrumental air flows. Errors in the experimental aerosol and sheath flow rates will propagate immediately into the derived particle number concentrations and/or particle sizes. Our general advice is to combine continuous and automated flow measurements inside the instrument with the manual precision measurements that are typically part of regular maintenance. To ensure continuous observations of the aerosol and sheath air flow, our recommended set-up includes the use of calibrated flow meters in the respective positions.

For the aerosol flow, we recommend using a calibrated differential pressure transducer measuring the pressure drop across a laminar flow element (capillary). While such a capillary can be manufactured from widely available plumbing elements, care should be taken to warrant an undisturbed laminar flow across the device. It is particularly not recommended to use mass flow meters for the aerosol flow, because of particle losses. The measured flow values should be recorded and stored with at least the same time resolution as the measured electrical particle mobility distributions. As a guideline for quality control, the continuously recorded aerosol flow should not deviate more than 5% from the set-point. Besides the continuous measurement, the aerosol flow needs to be checked manually using a precision volumetric flow meter (e.g. an electrical bubble flow meter). This manual measurement should take place as often as possible, but at least at each service occasion (every month at least). The quality of the continuous flow measurement will be improved if the differential pressure transducer is recalibrated regularly.

For the sheath air flow measurement, two options are possible: Either a differential pressure flow meter as described above, or a mass flow meter – because particle losses do not matter inside the sheath air flow. To capture the flow rate under conditions as close to the conditions (pressure, temperature) inside the DMA, the flow meter should be installed near the sheath air inlet (but upstream of the HEPA filter). For differential pressure flow meters, the sensor

voltage is typically calibrated against a reference volumetric flow. Any mass flow meter should also be calibrated for volumetric flow using a reference volumetric flow meter, thereby accounting for air pressure and temperature in the laboratory. As a guideline, the sheath air flow should be kept as constant as possible, with a maximum deviation of its floating average of 2% around the set-point value. The required temporal stability can be accomplished either by a critical orifice/pump set-up or by an air blower that is controlled by software or hardware.

### **Temperature and pressure**

To ensure the highest quality and traceability of mobility particle size spectrometer measurements, temperature and absolute air pressure should be monitored in the instrument. The objective is to determine the conditions given at any time inside the DMA, because these are needed to ascertain the correct sizing of the particles and to adjust the final particle number size distributions to standard conditions (273.15 K, 1013.25 hPa). The preferred option is to monitor temperature and absolute air pressure near the aerosol inlet of the DMA, however, without disturbing the laminar flow profile. Since RH sensors are usually capable of recording temperature as well, it is useful to store the temperatures values from those positions as well. As mentioned before, all parameters should be stored with at least the time resolution of the measured electrical mobility distribution. In the case of dual mobility particle size spectrometer, it is obligatory to report the recorded parameters separately in conjunction with each DMA.

#### *5.2.1.2 Recommended particle loss correction (method of equivalent length)*

Particle losses may practically occur in any part of a mobility particle size spectrometer. An important mechanism is particle diffusion to walls e.g. inside of pipes, the DMA, aerosol dryer and bipolar charger, especially for particles smaller than 100 nm in size. If particle losses in a particular device are known as a function of particle size, they can be corrected during the data post-processing. A useful parameter to describe particle losses in any component of the mobility particle size spectrometer is the method of "equivalent pipe length". Particle losses by diffusion of different components of the mobility particle size spectrometers are described by a straight pipe, which has the same particle penetration (equivalent pipe length, see Table 5.1). The losses can thus be easily computed for any particle size and flow rate from such an equivalent pipe length. Equivalent pipe lengths of different devices and plumbing elements aligned in sequence can be simply added if they are traversed by the same rate of aerosol flow. To ensure traceability of the data, any such corrections need to be documented when submitting data to a database. To avoid inconsistent datasets, manufacturer-based correction schemes should not be applied unless they have been verified as consistent with these recommendations by WCCAP.

### **Plumbing**

Particle losses by diffusion in a straight pipe can be described by analytical formulas derived for the laminar flow regime. For a developed laminar flow, these losses depend only on the pipe length, the flow rate through the pipe, and the particle size. When designing a mobility particle size spectrometer, it is advisable to use connecting pipes as short as possible, and as straight as possible.

Enhanced diffusional particle losses may occur in sampling pipes containing bends or elbows. These enhanced particle losses increase with a decreasing radius of the bend or elbow. We estimated the equivalent pipe length of a 90° bend based on the investigation of Wang et al. (2002). Using curves with smooth radii instead of elbow joints will also reduce the opportunity for particle losses. It is very essential that the plumbing consists of electrical conducting material, preferably stainless steel. Experience has shown that non-conductive tubing (e.g. plastics) may remove a considerable fraction of any charged particles by electrostatic forces.

**Bipolar diffusion charger**

Particle losses also occur inside bipolar diffusion chargers. The loss correction can be directly applied based on the experimentally determined penetration efficiency. Alternatively, any experimental penetration efficiency under a specific flow can be converted to an equivalent pipe length using the diffusional deposition formula for laminar flow. Particle losses for sub-10 nm particles across  $^{85}\text{Kr}$  bipolar diffusion chargers were measured for a custom-made bipolar charger.

**Differential mobility analyser**

Different DMA types exhibit different particle losses due to Brownian diffusion. The probability of a particle penetrating through a DMA depends on the losses in the DMA inlet and outlet region as well as on the transfer function in the DMA classification region. Short column lengths and high aerosol and sheath air flows are general design features that minimize particle losses. Particle losses can be either simulated by diffusional deposition models, or estimated experimentally. As with the bipolar diffusion charger, the diffusional losses across different DMAs have been simulated by an equivalent pipe length as given in Table 5.1.

**Table 5.1. Recommended equivalent lengths taken from Wiedensohler et al. (2012)**

Device	Equivalent pipe length	
Hauke-type medium-DMA (28 cm effective length)	4.6m	Karlsson and Martinsson (2003)
Hauke-type short-DMA (11 cm effective length)	4.6m	IFT internal calibration
TSI long-DMA (444mm effective length)	7.1m	Karlsson and Martinsson(2003)
TSI nano-DMA (49.9mm effective length)	3.64m	Jiang et al. (2011)
Permapure Nafion dryer SS2400	2.5m	Dick et al. (1995)
Permapure Nafion dryer SS1200	1.25m	Dick et al. (1995)
Diffusion dryer (e.g. TOPAS)	5m	estimated from Tuch et al. (2009)
90 bend (less than 5 cm radius)	0.15m	estimated from Wang et al. (2002)
Bipolar diffusion charger (IFT custom-made)	1m	Covert et al. (1997)

**5.2.1.3 Operation procedures and calibrations**

For long-term mobility particle size spectrometer measurements, we recommend the following listed items to improve the quality of the measurements and calibrations:

- Pressure transducers employed to measure the aerosol flow rate or mass flow meters used to determine the sheath air flow rate have to be calibrated at least twice a year. The aerosol and sheath air flow rates should be regularly measured once per month with an independent flow standard such as an electrical bubble flow. The reference standard should have a low pressure drop. The flow rate should be determined at the pressure within the DMA.
- In case of a closed-loop instrument, the pump/blower must be sealed and leak testing should be part of the regular maintenance schedule for the instrument.

- Humidity and temperature sensors for the aerosol and sheath air flow have to be checked prior to their deployment and afterwards at least once per year.
- The response function of the high voltage (HV) supply should be calibrated. This should include the analogue output module if the high voltage supply is controlled through an analogue voltage. The calibration function of the high voltage should be implemented into the scanning software or the data analysis. Correct sizing of small particles is highly sensitive to accurate knowledge of the applied HV. Particular care is, hence, required in the low voltage range. A HV-probe with ultralow impedance should be used here. The HV power supply has to be checked monthly.
- Furthermore, CPCs have to be calibrated regularly at least once per year to detect malfunctions such as degradation of the laser diode, temperature instabilities, or internal pollution. CPCs should be only used after determining the flow rate and after a calibration of the detection efficiency curve (see also Wiedensohler et al., 1997) and the plateau detection efficiency. Often, the CPC flow rate is controlled by a critical orifice. It should not differ more than few per cent from the nominal value. The deviation of the flow rate from the nominal value should then be taken into account in the calculation of the particle number size distribution. The volume flow rate should be checked on a monthly basis.
- The sizing accuracy of mobility particle size spectrometers has to be verified using 200 nm PSL spheres frequently. The use of 200 nm PSL particles is a compromise between obtaining a sufficient particle number concentration and a minimum of residual material on the particles. The measured peak diameter should be within the nominal uncertainties of the PSL spheres ( $\pm 2.5\%$ ) and the sheath air flow rate ( $\pm 1\%$ ). Due to a pressure drop over the external volumetric flow meter, it is often difficult to precisely measure the actual flow rate of the sheath air. In this case, the sheath air flow rate might be slightly adjusted by a few per cent to match the nominal PSL sphere size (sizing calibration).
- For "scanning" mobility particle size spectrometers, an incorrect pluming delay time can only be determined by the PSL sphere check. The pluming time is correct if up- and down-scans show the same result. The scan time has to be long enough because of the slow CPC response and to avoid smearing effects. We recommend an up- or down-scan time of minimum two minutes.
- Mobility particle size spectrometers should also be regularly compared to a reference instrument for a period of few days once per year (if a reference system is available). This intercomparison can be done either within an intercomparison at the calibration facility or at the sampling site.
- The total particle number concentration measured by a CPC can be compared to the number integral of the size distribution. The integral of the particle number size distribution should be compared to the directly measured total particle number concentration if no nucleation mode particles are present. Ideally, the difference in particle number concentrations should be smaller than 10% after correction for internal diffusional losses.
- Each CPC may have a rather individual particle counting efficiency, which can be determined experimentally. The size-dependent counting efficiency of an individual CPC depends on many specific factors, such as CPC geometry, or the actual supersaturation profile inside the condenser. If experimental data on the counting efficiency of a particular CPC are not available, the manufacturer's calibration curve can be applied with caution. Our recommendation is, however, to calibrate CPCs individually against a reference instrument.

- A zero-check of the system should be also done every month. An absolute particle filter should be connected to the system inlet and scanned for several size distributions. Ideally, the background should be close to zero.
- The DMA and the laminar flow element used to determine the aerosol flow rate have to be cleaned once per year. CPCs have to be serviced by an experienced person to clean the saturator and the optics.
- The bipolar diffusion charger should not be opened. The instructions of the manufacturer have to be followed.
- The mobility particle size spectrometers should be operated in an environment of 15-30°C to avoid a malfunction of the particle counter.

The time resolution of the measurements of particle number size distributions should be preferably maximum 10 minutes. The exact data submission protocol for these measurements is available at the WDCA.

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## CHAPTER 6. CLOUD CONDENSATION NUCLEI

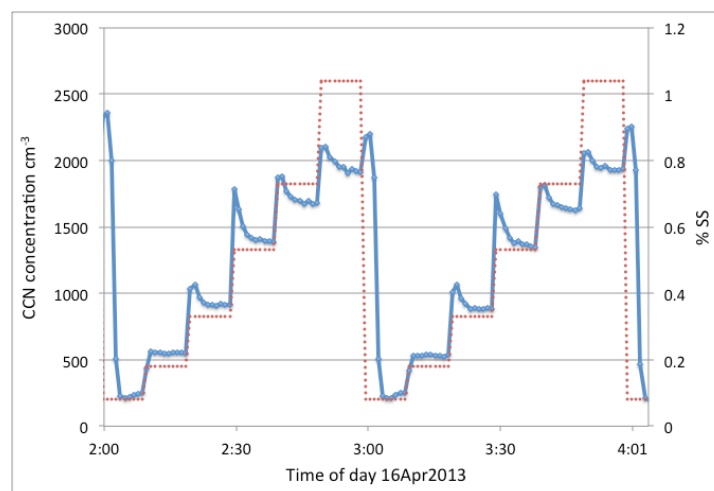
### 6.1 Introduction

Cloud condensation nuclei (CCN) are particles that are capable of activating to form cloud droplets at a given per cent super saturation (%ss). According to the Köhler equation, the vapour pressure or %ss above an aqueous drop will vary with the drop surface tension or size and the solute concentration and chemical composition. Measurements of CCN, along with cloud updraft velocity and liquid water content are important to model cloud droplet formation. Climate studies of the indirect radiative forcing need to know droplet number concentration and size to predict cloud lifetimes and albedo. The Droplet Measurement Technology (DMT) CCN (Roberts and Nenes, 2005) measures the CCN concentration over a range of %ss values and the resulting droplet size distribution in 21 size bins. Complimentary measurements of aerosol number concentration, size, composition and hygroscopic growth gRH measurements can be used further analyse CCN data. The recommendations here pertain to surface measurements of polydisperse aerosol using a single column DMT CCN and are in addition to those procedures recommended in the DMT operations manual.

### 6.2 Instrument operation

#### Time scale

For surface sites we recommend setting the time scale of data collection to coincide with changes in the air mass, other measurements at the site as well as typical times scales used by climate models. We recommend stepping the CCN %ss values through 60 minute sequences. The image below shows a typical sequence that steps through 6 different %ss values every 60 minutes with 10 minutes at each %ss value. For reliability and ease of data manipulation and merging with other datasets, start the scan sequence at the top of the hour so that the time after the hour of each %ss value does not change. If the scanning sequence is not set through an external serial port command then the operator will need to check the time sequence and restart the CCN programme at the top of the hour should the timing sequence change.



**Figure 6.1. Stepping scheme of %SS (red) and typical CCN number concentration (blue) on April 16<sup>th</sup>, 2013 at ARM site in Cape Cod, USA**

The duration of the measurement at each %ss value should be about 10 minutes or long enough to obtain a stable dT (T3-T1) value and good counting statistics (Figure 6.1). The extent of the CCN signal overshoot at the start of the dT change varies with the aerosol type, dT step size and column thermal properties. Usually at least 5 minutes is needed to

obtain a stable CCN concentration. A good range of %ss values is between 0.1 and 1.0. Concentrating the measurements at lower %ss values <0.5% ss is desirable as it mimics the %ss values often found in cloud updrafts. A typical stepping sequence is 0.1, 0.2 0.3, 0.5, 0.75, 1.0. A higher %ss value of 1.0 or slightly higher is needed to verify that the CCN concentration is comparable to the CN concentration and the instrument is operating properly. If the CCN signal is greater than the CPC signal this could indicate the CPC is clogged, a leak in the CCN, incorrect sample flow on either instrument or a poor sheath air filter on the CCN.

### **Flow rate**

The DMT CCN comes in a temperature scanning mode although the instrument can be modified for flow scanning (Moore and Nenes, 2009). For the temperature scanning mode the default sample:sheath flow ratio of 10 is recommended with a total flow of 500 cc min<sup>-1</sup>. A range of flow ratios from 7 to 12 will still produce acceptable data.

Often turbulence in the sample flow line creates noise in the sample and sheath flows, especially if the CCN picks off a much faster flow line or if the flow in the sample stack is turbulent due to high winds. A remedy for this is to have the CCN sample line flow through a large diameter line or mixing vessel to remove pressure fluctuations from the line. The default flow rate PID values are optimized for fast control of the flow proportional valve. The flow stability can be increased by optimizing the instrument PID values for a slower response in the DMT Service Tab. Refer to the DMT manual on how to optimize these values.

### **Instrument temperature stability**

Instrument error increases with instability in the inlet temperature as well as the sample RH. Use the default temperatures differences with  $T_1 < T_{inlet}$ . To minimize temperature instability keep the instrument away from air conditioners or heater vents. Keep the room temperature between 18 and 27 °C.  $T_{inlet}$  needs to be kept above the ambient dew point to prevent condensation in the sample inlet. Alternatively the sample air can be dried with a Nafion drier.

## **6.3 Data collection and processing**

### **Flags**

The standard deviation of the temperature gradient ( $T_3 - T_1$ ) is not in the standard serial output. We recommend adding this parameter in the post data processing as a means of judging whether the temperature gradient and hence %ss values are stable.

If the data are averaged over a %ss set point value, the unstable data at the beginning of the dT step change should be removed from the data average.

Add a flag if the sheath:sample flow ratio is outside the range of 7-12.

Add a flag if the data are contaminated or have instrument errors.

Add a flag if the total CCN number concentration exceeds 5000 cm<sup>-3</sup>. At high particle concentrations the instrument becomes water limited and a high fraction of the particles do not activate to droplets. Latham and Nenes (2011) present a correction scheme for the %ss decrease under conditions of CN concentrations greater than 5000 cm<sup>-3</sup>.

The CCN salt calibration information should be included in the file metadata. For consistency the instrument should be calibrated to the dT set point and not the actual  $T_3 - T_1$  value.

For calibrations performed at a pressure altitude different than the site location, the %ss salt calibration should be adjusted to the site ambient pressure. Rose et al. (2008) found the pressure dependence of the %ss to be about 0.037% per 100 hPa. Note that factory calibrations at DMT are done at a pressure altitude of about 840 hPa (Boulder, CO, USA).

## 6.4 Instrument maintenance

Note that these recommendations are in addition to those given in the DMT CCN manual. Please refer to the manual for maintenance, calibration information and procedures.

### Ceramic bisque maintenance

Long-term operation of the column leads to a degradation of the ceramic column and a build up of bacteria and mould in the tubing and column. The change in the column characteristics can alter the thermal resistance across the column and measurement accuracy. You can add a few drops of a weak antibacterial agent to the CCN supply water to discourage bacterial growth. We recommend flushing the ceramic column with a weak 5% household bleach solution in distilled water once a year for systems under continuous operation. **DO NOT flush the bleach solution through the Nafion humidifier or any of the system solenoid pumps.** The procedure below describes the bleach flush process. Refer to Figure 4 of the manual (Figure 3 in newer manuals), which shows the CCN Air/Water Flow Chart for tubing numbers.

- 1) Remove the OPC and plug the hole at the bottom of the column. This would be a good time to clean the OPC. Note there are two o-rings on the bottom plate above the OPC that will need to be in place when the OPC is put back in place.
- 2) Remove tube #17 from the solenoid pump leaving the other end attached to the bottom of the column. Check this tube for white deposits. A white deposit may indicate either bacteria in the line or ceramic deposits from column decay. Place the end of tube #17 into a drain bottle.
- 3) Disconnect the 1/8" tubing line (#11) that runs from the outlet of the Nafion nylon cross to the column water inlet at the Nafion cross. Make an adapter line that runs from this 1/8" tubing from the column water inlet (#11) to top of the supply bottle cap. The line should pass through the connector on the cap and to the bottom of the bottle. Make another adapter that runs from the other outlet of the supply bottle cap to either a hand-operated pump or a small compressor with a low flow. An aquarium pump works well for this purpose.
- 4) Place a weak solution of household bleach and distilled water (diluted to about 5%) in the supply bottle.
- 5) Pressurize the supply bottle to force the bleach solution through the column and into the drain bottle. Repeat the procedure twice more with distilled water to rinse the bleach solution from the column.
- 6) Replace the OPC and water tubing connections. Leak test the CCN instrument.

### Daily checks of the CCN operation

- 1) Refill distilled water in Supply bottle and empty water in Drain bottle.
- 2) Check for water in the small water trap bottle. Empty trap in water and check for water leaks.
- 3) Check that T2, T3 and Topc are stepping through the dT hourly schedule. Check that T1 and Tinlet are stable.
- 4) Check that the flows are set close to Total 500, Sheath 455, Sample 45. If the ratio of the Sheath/Sample flow is not between 9 and 11 then remove the instrument cover and turn the green knob on the manual flow valve until this ratio is ~10.
- 5) Check the reading of the 1<sup>st</sup> stage monitor on the OPC menu. If this value is > 0.5 then spray clean air into the OPC as directed in the CCN manual. Should the OPC become fogged with water make sure the water flow is set to low and the purge gas toggle switch on the printed circuit board is set to two seconds. If the monitor voltage remains high then turn off the liquid supply pump and wait several hours for the voltage to decline. If the voltage still remains high then turn off the CCN, remove the OPC and clean the optics.

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## CHAPTER 7. AEROSOL OPTICAL DEPTH

### 7.1 Introduction

Aerosol optical depth (AOD) is a quantitative measure of the vertically normalized extinction of direct solar radiation by scattering and absorption of aerosols between the point of observation and the top of the atmosphere. It is a measure of the integrated columnar aerosol load and therefore the single most important aerosol parameter for determination of the direct radiative effect (and forcing). AOD can be determined from the ground through solar attenuation measurements with sunphotometers (radiometers pointed at the sun) at solar sub-spectral regions, where attenuation by atmospheric trace gases is negligible. Usually AOD is determined at different solar spectral wavelengths, because the AOD spectral dependence contains information on size so that, for example, fractions of AOD attributed to sub- and supermicron size particles can be estimated. A more sophisticated sampling method with multi-spectral instruments, so that in addition to AOD measurements also the sky radiance is captured, allows additional, column-average, aerosol properties to be derived using inversion methods. These include particle size distribution in the optical sensitive range (0.05-15  $\mu\text{m}$  radius), information of aerosol shape (spherical or non-spherical), and the refractive indices at the sensing wavelengths. The imaginary part of the refractive index quantifies aerosol absorption, where absorption estimates are more reliable if AOD values are larger.

AOD is the single most comprehensive variable to assess the total aerosol load of the atmosphere and represents the least common denominator by which ground based remote sensing, satellite retrievals and global modelling of aerosol properties are compared. Ground based AOD attenuation measurement are highly accurate, unlike estimates from satellite retrievals. These satellite retrievals usually extract AOD from small changes in directional solar reflection over usually insufficiently accurately defined (surface reflection) backgrounds. Thus ground-based AOD observations are indispensable for the calibration and validation of AOD retrievals from satellites. Since the conversion of reflected sunlight into AOD also depends on aerosol size and absorption, the supplementary column information offered from attenuation measurements (Ångström exponent, fine-mode AOD fraction estimate) and from sun-/sky-inversions (absorption, shape and detailed size-distributions) is very useful to test retrieval models or evaluate model simulations in more detail.

AOD directly relates to a solar sub-spectral atmospheric transmission. The solar irradiance  $I$  at a given wavelength can be expressed as  $I = I_0 \exp(-m\delta) = I_0 \exp(-\delta/\cos(z))$  with  $I_0$  the extraterrestrial (top-of-the-atmosphere) spectral irradiance of the sun (which is well defined by location and time),  $\delta$  the (vertically normalized) optical depth and  $m$  the optical air mass factor, which describes the extended path compared to the nadir direction. At sun-elevations larger than 10 degrees above the horizon  $m$  is defined by  $1/\cos(z)$ , with  $z$  the solar zenith angle. If there is no atmospheric scattering (air-molecules, clouds) and/or absorption (trace gases, clouds) in the selected solar sub-spectral region then  $\delta = \text{AOD}$ . Thus, solar sub-spectral bands for AOD measurements are preferred where aerosol radiation interactions can be neglected or are easily quantified (e.g. scattering by air-molecules, commonly referred to as Rayleigh scattering).

If other atmospheric properties also affect solar scattering and absorption, the retrieval of AOD gets more complicated. Then, the total optical depth  $\delta = (\log(I_0) - \log(I))/m$  at a given wavelength is composed of several components such as scattering by gas molecules,  $\delta_R$  (Rayleigh scattering), extinction by aerosol particles,  $\delta_A$  or AOD, absorption by trace gases,  $\delta_G$ , e.g. ozone and nitrogen dioxide and possible cloud contamination  $\delta_C$ . In this case, AOD is obtained from the total optical depth by subtracting measured or modelled estimates of all other components  $\delta_A = \delta - \delta_R - \delta_G - \delta_C$ .

There are several regional AOD networks as well as some networks with global coverage (WMO, 2005). AERONET (AERosol RObotic NETwork) (Holben et al., 1998, 2001) is the major global sunphotometer network. It integrates several hundred identical sunphotometers with

added sky-scanning capabilities. AERONET uses a common protocol where data are sent immediately to a central processing unit, so that data products are available on the web (<http://aeronet.gsfc.nasa.gov>) within hours. Regular monitoring and regular calibration requirements assure high quality and site intercomparability. Other networks have special foci, such as GAW-PFR (precision filter radiometer) (Wehrli in WMO, 2005) focusing on background stations, SurfRad (Surface Radiation Budget Network) (Augustine, 2008) focusing on sites in the US and SKYNET (Sky Radiometer Network) focusing on eastern and southern Asia and in Europe (Nakajima et al., 2003). Each of these networks has less than 50 sites and data are stored in separate archives, when data access often is available only after significant delay. The most complementing network to AERONET is SKYNET, since their radiometers can also operate in the sky-radiance mode so that identical inversion methods can be applied for estimates of aerosol size detail and aerosol absorption.

## **7.2 Methods of measurement**

### **7.2.1 Wavelengths and field of view**

Measurements of the direct beam solar irradiance should be made at least at three different wavelengths from the list of centre wavelengths recommended by WMO (1986): 368, 412, 500, 675, 778, 862 nm and with a bandwidth of 5 nm. The spectral sub-bands were picked to assure a strong aerosol signal, to avoid major contaminations by trace gas absorption and to cover a spectral range so that general aerosol estimates are possible. The GAW-PFR network is using four AOD channels at 368, 412, 500 and 862 nm. While some other networks prescribe different wavelengths based on their specific needs (validation of satellite sensors, modelling efforts), measurements at  $500\pm 3$  nm and  $865\pm 5$  nm are typically available in most networks. AERONET uses narrow solar spectral bands centred at 340, 380, 440, 500, 670, 870, 940 (for water vapour) and 1020nm (with additional narrow spectral bands at 410 and 1600nm in new test instruments). For the AERONET inversions at 440, 670, 870 and 1020nm, direct attenuation and almucantar scan data (in both directions) are required for all four wavelengths. The field-of-view geometry for direct beam radiometers should correspond to the WMO (2008) specifications of a full opening angle of  $2.5^\circ$  and a slope angle of  $1^\circ$ . In addition to filter radiometers, various direct sun pointing spectroradiometers are used in order to determine AOD (e.g. Brewer (UV), Pandora (UV-VIS), Precision Spectroradiometer (UV-VIS-NIR), providing spectral information of AOD measured in narrow spectral band centres.

### **7.2.2 Sampling strategy**

Network independent measurements should be taken with a sampling rate of once every minute in order to allow for objective quality control and cloud filtering algorithms. This condition precludes the use of hand-held sunphotometers for routine observations, and limits their application to special programmes, e.g. ship-born campaigns (Smirnov et al., 2009).

Measurements are to be taken as instantaneous observations, i.e. with an integration time much shorter than the sampling rate, rather than averaging the signal over the sampling interval. This specification stems from the need to associate each observation with a specific optical air mass during the retrieval of AOD values, and that the solar zenith angle may vary rapidly when it is large.

A timestamp, given in UTC, should be recorded for each instantaneous observation. The data acquisition clock should be accurate or traceable to UTC within  $\pm 5$  seconds.

Dark signals should be measured as part of the sampling strategy, too. For instruments that are not equipped with a shutter or a 'dark' filter, dark measurements can be taken at night or simply by blocking the entrance aperture at least once per day.

Spectral radiation measurements taken under a network protocol may use different sampling strategies. AERONET (Holben et al., 1998) samples the direct attenuation typically every 15

minutes as a sequence of 3 measurements within 1 minute. Sky radiance data are sampled every hour but at higher frequency at sunrise and sunset (each half air-mass factor change).

### 7.2.3 Ancillary measurements

Atmospheric pressure is required for calculating the Rayleigh optical depth above the AOD observing site. Pressure should be accurate to better than 3 hPa in order that the uncertainty of the Rayleigh correction remains below 0.0025 optical depths. As Noon time pressure on 'clear days' may exceed the daily or annual average by more than 3 hPa, collocated measurement at hourly or better resolution are required.

At least daily values of total ozone are required to properly account for ozone absorption at wavelengths in the Chappuis band. At 500 nm and 675 nm, ozone optical depth amounts to about 0.01 for a column concentration of 300 DU. Total ozone values of a nearby Dobson or Brewer station may be obtained from the World Ozone and Ultraviolet Data Centre (<http://www.woudc.org>). Satellite overpass data of the Ozone Monitoring Instrument (OMI) can be obtained in near-real-time at <http://ozoneaq.gsfc.nasa.gov>.

## 7.3 Instrumentation

The CIMEL<sup>1</sup> sky-scanning radiometer, used in the AERONET network, has 8 channels. It comes with a data acquisition and control unit and is mounted on a dedicated sky-scanning robot. A similar instrument is used in SKYNET and offered by Prede<sup>2</sup>. Both instruments are more sophisticated than traditional sunphotometers in that they also measure sky radiances. Classic filter radiometers are offered by Carter-Scott Design<sup>3</sup>, PMOD<sup>4</sup>, YES<sup>5</sup> or EKO<sup>6</sup> and require a separate (not part of the radiometers) solar tracker and data acquisition system. Yankee Environmental Systems also offers multi-filter rotating shadowband (MFRS and UVMFRS) radiometers that come with a data acquisition and control unit and do not need a tracker. MFRS (visible range) and UVMFRS (ultraviolet range) radiometers can obtain direct beam irradiance as the difference between global and diffuse measurements, normalized by the solar zenith angle. There are also hand-held direct sun filter radiometers (microtops model) manufactured by Solar light<sup>7</sup> that sun-tracking requires manual operation and are ideal for measurements on moving platforms (e.g. on ships). Quality-control issues have plagued previous network operations with hand-held filter radiometers (e.g. BAPMoN), and their use at GAW stations is not recommended without a rigorous quality control and quality assurance programme. In addition, traditional spectroradiometers (e.g. Brewer instruments) have been used for AOD retrieval using direct sun measurements that are also used for other traces gases retrievals (e.g. total column ozone). Finally, spectroradiometers with sun tracking systems e.g. the Precision Spectroradiometer, constructed in PMOD-WRC Switzerland and the Pandora system by SciGlob<sup>8</sup>, are able to provide spectral AOD retrievals.

All types of above filter radiometers are suitable for AOD measurements at GAW stations. Comparisons of different co-located instruments (Mc Arthur et al., 2003, Mitchell and Forgan, 2003, Kim et al., 2008, Che et al., 2008) have demonstrated good agreement in the order of 0.01 optical depths between direct pointed instruments, and in the order of 0.015 for shadow band radiometers.

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<sup>2</sup> PREDE Co., 1117 Kusabana Akiruno-shi, 197-0802 Tokyo, Japan <http://www.prede.com>

<sup>3</sup> Carter-Scott Design, 16 Wilson Avenue, Brunswick. Victoria 3056 Australia <http://www.carterscott.com.au>

<sup>4</sup> PMOD, Dorfstrasse 33, 7260 Davos Dorf, Switzerland, <http://www.pmodwrc.ch>

<sup>5</sup> Yankee Environmental Systems, Inc., 101 Industrial Boulevard, POB 746, Turners Fall, MA 01376, U.S.A., <http://www.yesinc.com>

<sup>6</sup> EKO Instruments Trading Co, Sasazuka Centre Bldg. 2-1-6, Shibuya-ku, 151-0073 Tokyo, Japan, <http://www.eko.co.jp>

<sup>7</sup> Solar Light Company, Inc. 100 East Glenside Avenue Glenside, PA 19038, USA <http://solarlight.com/>

<sup>8</sup> SciGlob Instruments and Services, LLC 4656 Tall Maple Court Ellicott City, MD 21043 USA, <http://sciglob.com/index.html>

## 7.4 Calibration issues

Under conditions of low aerosol loadings, e.g. AOD  $\approx 0.05$  at 500 nm, a calibration error of 1% can result in an error of 12% for the daily mean AOD and even higher around noontime. WMO has recommended (WMO, 1994) an absolute limit to the estimated uncertainty of 0.02 optical depths for acceptable data and  $<0.01$  as a goal to be achieved in the near future. These specifications require a calibration uncertainty of better than 2% to be maintained for spectral radiometers in daily, operational use. As the sensitivity of sunphotometers and spectral radiometers tends to deteriorate with time, these instruments should be calibrated annually. Usually this means that the radiometer has to be removed from the station for a period of several weeks to months.

Most of the spectral radiometers for AOD are calibrated in terms of their extraterrestrial value  $I_0$ , i.e. the value they would read at the top of the atmosphere. It can be obtained by logarithmic extrapolation  $\ln(I(m)) = \ln(I_0) - m\delta$  of a number of measurements  $I(m)$  taken on the ground at different optical air masses  $m$  to air mass  $m=0$ . This method is commonly known as Langley-plot in honour of S. P. Langley who first used it in 1910. Langley-plot calibrations rely on high temporal and spatial stability of the optical depth  $\delta$  during the calibration process, conditions that are hardly found at a given observing site, unless at high altitudes, thus precluding reliable on-site calibration of individual instruments. Many variations of the classic Langley-plot (e.g. Herman et al., 1981, Forgan, 1994, Schmid and Wehrli, 1995) were devised over the years. However, even statistically perfect regressions may result in erroneous  $I_0$  due to systematic variations of  $\delta$  during the calibration (Shaw, 1976). These errors can only be overcome by averaging a sufficiently large ( $>20$ ) number of Langley-plots while assuming a normal distribution of systematic variability in  $\delta$ . Thus, the Langley method is often restricted to the calibration of a selected instrument which then serves as standard for side-by-side calibration of multiple field radiometers of the same type. In addition, there are modified Langley techniques (e.g. SKYNET) that they retrieve by in situ procedures (Campanelli et al. 2004).

Spectral radiometers at GAW stations can be calibrated by comparison to either a travelling standard or to a group of standard radiometers at a regional or world calibration centre. The World Optical Depth Research and Calibration Centre (WORCC) is providing calibration for PFR instruments. AERONET is providing calibration services for the Cimel instrument.

## 7.5 Data evaluation

The majority of AOD observations are organized in one of the global networks (see Introduction) and adhere to protocols and evaluation schemes defined by these networks. Individual stations or national networks which are not or may not become associated with one of these networks may find a selection of commonly used algorithms in the following sections.

The observed radiometer signal is described by the Bouguer-Lambert-Beer law:

$$S(\lambda, m, R) = S_0(\lambda)e^{-m\delta(\lambda)}R^{-2} + \varepsilon$$

where  $S_0$  is the exoatmospheric signal at wavelength  $\lambda$  and standard Sun-Earth distance  $R$  of 1 astronomical unit,  $m$  is the optical air mass along the line of sight to the Sun,  $\delta$  is the total optical depth, and the term  $\varepsilon$  accounts for the circumsolar sky radiance in the field of view of the sunphotometer. The total optical thickness  $m\delta$  includes several terms  $\delta_i$  describing the extinction by different atmospheric components: molecular scattering, gas absorption and aerosol extinction. As these components have different vertical structures, their optical air mass along a refracted slant path through the atmosphere are usually slightly different. Therefore, the total optical thickness has to be written as  $\tau = m\delta = \sum m_i\delta_i$ .

Taking the logarithm of the Bouguer-Lambert-Beer equation above and re-arranging terms leads to the basic equation for the determination of aerosol optical depth  $\delta_A$



$$\delta_A = \frac{\ln(S_0) - \ln(S - \varepsilon) - 2 \ln(R) - \sum \delta_i m_i}{m_A}$$

where the subscript  $A$  indicates aerosol specific terms and subscript  $i$  stands for individual components of atmospheric extinction.

In the last equation, the signal  $S$  is the only measured quantity, all other terms are based on models of atmospheric extinction or of the measurement process that are approximated by relatively simple expressions for practical use.

### **7.5.1 Solar elevation**

The solar zenith angle  $\zeta$  is required in the calculation of air mass factors  $m_i$ . It may, together with the Sun-Earth distance  $R$ , be calculated by the algorithm given in (Michalsky, 1988), and also in (WMO, 2008).

### **7.5.2 Rayleigh correction**

Rayleigh optical depth  $\delta_R(\lambda)$  can be accurately approximated by the algorithm given in (Bodhaine et al., 1999). The corresponding air mass  $m_R$  may be calculated by the revised Kasten formula (Kasten and Young, 1989).

### **7.5.3 Ozone correction**

The ozone optical depth  $\delta_{O_3}(\lambda) = a_{O_3}(\lambda)c$  can be calculated from the spectral absorption coefficient  $a_{O_3}(\lambda)$  and the total ozone content  $c$ . A useful table of ozone absorption coefficients at fixed temperature (228K) is given in (Gueymard, 1995). For total ozone concentration  $c$  see section 7.2.3 above. The corresponding optical air mass  $m_{O_3}$  may be calculated by formula (6) in (Komhyr et al., 1989).

### **7.5.4 Circumsolar stray light correction**

Spectral radiometers inevitably receive some circumsolar stray light in their finite field of view. The observed radiometer signal  $S$  is thus increased by a diffuse component  $\varepsilon$  leading to an underestimation of the optical depth. This circumsolar radiation is proportional to the aerosol optical depth and strongly dependent from the aerosol scattering phase function. An empirical model for a wide range of realistic aerosol types is given in (Russel et al. 2004) as correction factors for initial (underestimated) aerosol optical depths.

### **7.5.5 Aerosol airmass $m_A$**

As the typical scale heights for aerosol concentration are comparable to the scale height of water vapour, the Kasten formulation for water vapour optical air mass by (Kasten, 1966) may be used during periods of low stratospheric aerosol load.

### **7.5.6 Nitrogen dioxide correction**

$\text{NO}_2$  can affect AOD retrieval at certain wavelength bands with high  $\text{NO}_2$  absorption. It can be calculated using  $\text{NO}_2$  absorption coefficients and the total  $\text{NO}_2$  content (measured from satellite sensors or using  $\text{NO}_2$  climatology).

## **7.6 Quality control and assurance**

Quality Control (QC) of routine measurements should include checks of the cleanliness of the optical window, of the accuracy of the solar tracker and, in the case of non-tracking shadow

band instruments, checks of the horizontal levelling. All adjustments made or malfunctions detected should be recorded in a logbook and archived together with the raw measurements. Further QC involves data screening during the evaluation process, especially flagging measurements for suspected cloud contamination in the line-of-sight.

Cloud screening is a notoriously difficult process as optically thin clouds are not readily distinguishable from optical depth associated with coarse mode aerosols. Several authors (e.g. Harrison and Michalsky, 1994; Smirnov et al., 2000; Alexandrov et al., 2004, Kaufman et al., 2006) have proposed algorithms based on various assumptions about the physical, temporal, or spectral differences between aerosols and clouds.

Quality Assurance (QA) for AOD data mainly consists of maintaining proper calibration of the extraterrestrial signals within the required uncertainty of 1-2%. Rotating shadowband radiometers need additional calibration of their angular response function as they do not match the ideal (cosine) response. As filter radiometers tend to show individual ageing effects, it is difficult to recommend a single recalibration interval, which could be from twice a year to every two years. Reprocessing of past data may become necessary to account for instrumental drifts between calibrations.

## 7.7 Reporting interval

The WDCA expects regular annual data to be reported as hourly statistics including arithmetic mean and standard deviation, median value, and number of measurements formatted as EBAS NASA-AMES files. WDCA also accepts raw or processed data in native time resolution. Further information can be found under:

<http://www.gaw-wdca.org/SubmitData/AdvancedDataReporting.aspx>

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## CHAPTER 8. GAW AEROSOL LIDAR

### 8.1 Introduction

Lidar (LIght Detection And Ranging) observations of the scattering of aerosols along a path traversed by a vertically-directed pulse of laser light are the best source of routine information on the vertical distribution of aerosol scattering and other physical properties. Aerosol balloon sondes instruments and aircraft measurements are not yet widely available, are less economical and therefore are not yet being conducted in many locations. Lidars operated from ground-based networks and from satellites are in place now. They can complement ground-based in situ or total column aerosol measurements. Ground-based lidars fill the ongoing need for insight into the structure of the boundary layer, its height, and its variability with time that is useful in understanding the representativeness of ground-based measurements. Furthermore, information on long-range transport in the free troposphere, cloud observations including cirrus clouds, and knowledge of the vertical distribution of light extinction due to aerosols are essential for understanding the climate role of atmospheric aerosols. For many climate processes (e.g. radiative transfer) altitude-resolved information about aerosols is essential.

Lidar observations are much more powerful when used in coordinated networks. Lidar networks are fundamental to study aerosol on large spatial scale and to investigate transport and modification phenomena. There are several research lidar networks which are contributing to GAW: Ad-NET, ALINE, CISLiNet, EARLINET, MPLNET, and NDACC. These networks are coordinated within GALION, the GAW Aerosol Lidar Observation Network. GALION is a network of networks as it is not feasible to implement a global aerosol lidar network by installing a homogeneous set of systems at a number of stations selected for optimal coverage. Instead GALION makes use of existing systems at established stations, of the experienced operators of these systems, and of existing network structures. The structure and development of GALION is described in the GAW Report No. 178.

In summary, there is a need for systematic measurements of the vertical aerosol distribution by ground-based lidar systems at GAW stations. It is recommended that lidar systems should be installed where a comprehensive aerosol programme has been implemented, especially those with strong measurement research programmes that support long-term monitoring. The integration of aerosol lidar observations with other measurements by radiosonde, ozone sonde, sunphotometer and satellite is most useful allowing for a maximum synergy of information.

### 8.2 Lidar remote sensing

Remote sensing by lidar has received wide application in the space- and time-resolved investigation of atmospheric trace constituents, clouds, wind and temperature since its invention. Today lidars are used as ground-based systems, on airborne platforms, and even from space (LITE experiment, CALIPSO, launched in 2006, and the next planned missions ADM-Aeolus and EarthCARE). Since the pioneering work by Fiocco and Grams (1964) to investigate stratospheric aerosols, numerous Lidars have been built with increasing specialization to meet the growing need in research and environmental control. This relatively young science has now arrived at the point where systems can be designed for certain purposes and built with high reliability and durability. Rapid progress in laser technology, measurement technique, and data acquisition support this development. Lidar systems for some specific applications are now commercially available.

Lidar measurements of aerosols may be used in a twofold way when applied at GAW stations. Firstly, they will provide high-resolution information on the altitude dependence in the occurrence of tropospheric aerosols, including the retrieval of optical properties such as aerosol backscatter and extinction. Secondly, this information can then be used to derive variations of the atmospheric structure and transport phenomena by interpreting the aerosols as tracers of such variations.

### 8.3 Aerosol lidar techniques

The basic lidar principle is the following: a laser pulse is transmitted into the atmosphere where it encounters gas molecules and particles; a small amount of this energy is backscattered in the direction of the receiver system, typically a telescope, and transferred to a photodetector as a photo-multiplier. The resulting electrical signal is proportional to the optical power received, which depends on the presence, range and concentration of atmospheric scatterers and absorbers in the light path volume.

Lidar techniques are able to characterize atmospheric aerosols in terms of vertical profiles of extinction and backscatter coefficients, lidar ratio, optical depth and microphysical properties such as shape, refractive index and size distribution. Several different lidar techniques exist, depending on the specific instrument design and mainly on the specific laser-atmosphere scattering process.

Elastic backscatter lidar is the simplest type of aerosol lidar: the backscattered wavelength is identical to the transmitted wavelength, and the magnitude of the received signal at a given range depends on the backscatter cross-section of scatterers along the path to that range. Typical operating wavelengths are 355, 532, 1064 nm. The typical product of a backscatter lidar is the vertical profile of the aerosol backscatter coefficient obtained assuming a lidar ratio, i.e. the extinction-to-backscatter ratio, mostly constant throughout the profile and usually derived from existing climatology obtained with measurements from Raman lidar, described later. In this sense it is necessary to underline that without an a-priori assumption about the lidar ratio, these kind of lidar systems cannot provide quantitative aerosol backscatter data.

Depolarization lidars are elastic backscatter lidars equipped with channels for the detection of the 2 parallel and cross-polarized components of the backscattered radiation. This provides quantitative information about particle shape, strongly contributing to aerosol typing as well as to the identification of thin clouds contaminating the profiles. Typical operating wavelengths are 355 and 532 nm. Depolarization lidar systems need accurate calibration.

The Raman lidar technique operates by measuring the inelastic Raman scattering by a specific gas. The Raman backscattered radiation from molecular nitrogen (or oxygen) is typically used for retrieving the vertical profile of aerosol extinction coefficient that, coupled with the elastic scattering collected at the same emission wavelength, provides also the vertical profile of the aerosol backscatter coefficient with no assumption on the lidar ratio. Typical operating wavelengths are 355 and 532 nm even though during daytime conditions the use of ultraviolet wavelengths is preferred for the higher signal-to-noise ratio achievable with respect to the visible. Most of the existing Raman lidar instruments are also equipped with a depolarization channel providing data on particle linear depolarization ratio. Moreover, advanced multi-wavelength Raman aerosol lidar techniques have been demonstrated to be the only technique capable of providing range-resolved aerosol microphysical properties. Moreover rotational Raman lidar systems can be designed for optimizing extinction measurements in daytime conditions.

The High Spectral Resolution Lidar (HSRL) technique provides calibrated measurements of aerosol optical depth, extinction and backscatter. Measurements are computed from ratios of the particulate scattering to the measured molecular scattering. This provides absolute calibration and makes the calibration insensitive to dirt or precipitation on the output window. A very narrow, angular field-of-view reduces contamination from spurious sources, like multiple scattering contributions. The small field-of-view, coupled with a narrow optical bandwidth, nearly eliminates noise due to scattered sunlight improving the single-to-noise ratio also during daytime operations.

Ceilmeters are basically elastic backscatter lidars that employ a diode laser source emitting at infrared wavelengths (typically 905 or 1064 nm) using a low energy but a high repetition rate (order of  $\mu\text{J}$  of energy per pulse and kHz of rate) and detect the elastic backscattered radiation

by clouds and precipitation. Ceilometers are a self-contained, 'turn-key', ground-based, active, remote-sensing device designed to measure cloud-base height and potentially the backscatter signals by aerosols. Ceilometers can provide qualitative information about aerosol vertical distribution.

All these lidar techniques can provide data products suitable for monitoring the spatial and temporal distribution of aerosols up to the upper troposphere / lower stratosphere region and can characterize them from a dynamical and microphysical point of view. The main lidar limitation is related to the presence of rain, dense fog and thick clouds (optical depths larger than 2-3) that do not allow monitoring of the atmosphere above the cloud base region. Altitude range covered by the lidar instruments is limited at the bottom from the overlap height (altitude where there is a full overlap between the transmitter and the receiver) that it is typically about 250-500 meters above the ground level but could be also up to 2 km above the ground depending on the specific design. The maximum altitude range strongly depends on the laser power and optical design.

#### 8.4 Lidar aerosol products

Lidar aerosol products:

- Geometrical properties
  - layer identification (top, bottom and centre of mass)
- Optical properties profiles:
  - Extensive optical parameters: aerosol backscatter coefficient ( $b_a$ ), aerosol extinction coefficient ( $a_a$ )
  - Intensive optical parameters: Lidar ratio ( $S$ ), particle linear depolarization ratio ( $d_a$ ), Ångström backscatter related exponent ( $\alpha_b$ ), Ångström extinction related exponent ( $\alpha_a$ ) Optical properties in the identified layer
  - Integrated backscatter, AOD
  - Mean intensive optical parameters (Lidar ratio, particle linear depolarization ratio, Ångström backscatter related exponent, Ångström extinction related exponent)
- Aerosol typing classification
- Mass concentration estimate
- Microphysical properties retrieved

Table 8.1 reports the different aerosol lidar products that can be obtained with the different lidar techniques as listed below.

Lidar techniques for aerosol monitoring:

- Ceilometer
- Single-wavelength backscatter lidar
- Single-wavelength backscatter lidar + depolarization channels
- Raman lidar
- Raman lidar + depolarization channels
- High Spectral Resolution Lidar (HSRL)
- High Spectral Resolution Lidar (HSRL) + depolarization channels
- Multi-wavelength backscatter lidar
- Multi-wavelength backscatter lidar + depolarization channels
- Multi-wavelength Raman lidar
- Multi-wavelength Raman lidar + depolarization channels

**Table 8.1. Lidar products related to specific ground-based lidar techniques**

Ground-based Lidar techniques	Geo. properties	$b_a$	$a_a$	$S^*$	AOD	$\hat{a}_a$	$\hat{a}_b$	type <sup>‡</sup>	Microphys. prop.
ceilometer <sup>‡</sup>	✓	✓ <sup>§</sup>							
Ceilo+sun photo.	✓	✓	✓(d) <sup>6</sup>		✓(d)				
Ceilo+sun photo.+ depol	✓	✓	✓(d) <sup>1</sup>		✓(d)			✓ (limited)	
Backscatter lidar 1- $\lambda$	✓	✓							
Backscatter lidar 1- $\lambda$ + sun photo.	✓	✓	✓(d) <sup>1</sup>		✓(d)				
Backscatter lidar 1- $\lambda$ + sun photo.+ depol	✓	✓	✓(d) <sup>1</sup>		✓(d)			✓(d) (limited)	
Backscatter lidar m- $\lambda$ <sup>#</sup>	✓	✓					✓		
Backscatter lidar m- $\lambda$ <sup>#</sup> + sun photo.	✓	✓	✓(d) <sup>1</sup>		✓(d)	✓(d) <sup>1</sup>	✓		✓(d) <sup>1</sup>
Backscatter lidar m- $\lambda$ <sup>#</sup> + sun photo.+ depol	✓	✓	✓(d) <sup>1</sup>		✓(d)	✓(d) <sup>1</sup>	✓	✓	✓(d) <sup>1</sup>
1- $\lambda$ Raman lidar/HSRL	✓	✓	✓ <sup>7</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>			✓ <sup>2</sup> (limited)	
1- $\lambda$ Raman lidar/HSRL +sun photo.	✓	✓	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓(d) <sup>1</sup>	✓(d) <sup>1</sup>	✓ (limited)	✓(d) <sup>1</sup>
1- $\lambda$ Raman lidar/HSRL +sun photo.+ depol	✓	✓	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓(d) <sup>1</sup>	✓(d) <sup>1</sup>	✓	✓(d) <sup>1</sup>
m- $\lambda$ <sup>#</sup> Raman lidar	✓	✓	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓	✓ <sup>2</sup>	✓ <sup>2</sup>
m- $\lambda$ <sup>#</sup> Raman lidar +sun photo.	✓	✓	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓	✓	✓ <sup>2</sup>
m- $\lambda$ <sup>#</sup> Raman lidar +sun photo.+ depol	✓	✓	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓ <sup>2</sup>	✓	✓	✓ <sup>2</sup>

\* From 2 independent measurements

‡ Identification of scattering type (aerosol particles, cloud droplets, ice crystals, some aerosol type information)

‡ A ceilometer is a single-wavelength, low-power lidar, with lower S/N ratio

§ if calibrated

<sup>6</sup> Estimate only

<sup>#</sup>  $m > 2$

<sup>7</sup> Most Raman lidar systems operate during night-time. 24h Raman lidar systems exist and their operability has been proved, however few systems nowadays operate Raman channels also during daytime; HSRL is independent of daytime.

d= only daytime, n= only nighttime



## Remarks:

- Range: typical altitude range is 0.3-15 km. The altitude range strongly depends on the optical design of the system and the laser power. More powerful systems are designed also for stratospheric measurements, in this case maximum altitude range is typically 25-30 km. Minimum altitude is limited by the overlap function which is strictly related to the specific optical design: specific designed systems have minimum altitude range at about 150 m.
- Resolution: vertical (meters), temporal (minutes)
- Accuracy: it is difficult to provide general estimation for the accuracy of the different lidar products because these strongly depend on the specific system and also on the meteorological conditions. On average, uncertainties for extinction and backscatter coefficient are about 20% (in case of Raman lidar or HSRL). Retrieval of microphysical properties is possible only if optical data have uncertainties lower than 20-30%.
- Limitation: lidar and ceilometer do not deliver aerosol products during rain, fog, low clouds.
- Ceilometers: there are several types of ceilometers in use in the meteorological community. Generally spoken, older and typically less powerful instruments are almost unable to detect aerosol layers in the atmosphere while newer instruments are quite useful for volcanic ash/dust detection and ash/dust plume tracking.
- A depolarization channel allows discrimination of volcanic ash and other aerosol particles. The Angström parameter has also been shown useful for this purpose.
- Discrimination of volcanic ash and dust/sand needs a depolarization channel together with a Raman channel and analysis of the Angström parameter.

## 8.5 Specifications

For all GAW lidars, calibration, data processing, and quality control measures need to be defined and standardized.

Recommended specifications can be summarized as follows: Single, mid-visible wavelength; day and night measurements of backscatter (basic systems), and depolarization (improved systems); range at least to the tropopause; compact and weather-proof housing; Raman or HSRL for extinction retrievals (improved systems); multiwavelength Raman or HSRL + depolarization channel(s) (advanced systems).

The sensitivity of the lidar should allow the retrieval of tropospheric optical depths in the range 0.02 - 2.0.

It is recommended that a basic GAW lidar system should comply with the following specific properties:

### Physical properties

- Lidar: robust, compact, low power consumption, stable optics, easy to adjust, operate, control and maintain.
- Housing: compact with window, window cleaning for unattended operation, weather-proof, humidity and temperature controlled.
- System (at least with some versions) transportable for special studies and intercomparisons.

### Transmitter

- For single-wavelength lidar systems, the mid-visible wavelength (close to sunphotometer channels) is recommended.

- The use of additional wavelengths (e.g. 1064 nm and/or 355 nm) is highly recommended for an advanced aerosol programme. It has been well established that it is often possible to derive extra information from multi-wavelength backscatter and depolarization data, including particle shape and size.

#### Safety

- Eyesafe emission (from out of the window) or use of safety devices such as radar and aircraft-tracing camera.

#### Mode of operation

- Operation: day and night use, continuous, automated operation
- Time resolution: averaging period down to minutes
- Height resolution: 30 m or better
- Range: from ground to a few kilometres above the tropopause

#### Signal

- Backscatter: minimum 1 channel for elastic Rayleigh + Mie backscatter
- Depolarization (recommended option for improved systems): two channels for co-polarized and cross-polarized signal for depolarization measurements
- Extinction (Raman or HSRL) (recommended option)
- Background: accurate measurement of background signal by pre-trigger and/or analysis of data from very far range

#### Close range signal

- To bring the minimum height for measurements down closer to ground one can add a low-altitude, wide field-of-view channel, or add scanning in elevation angle to near horizontal. Another possibility is to measure directly the lidar overlap function.

#### Communication

- System control: on-site and remote
- Data transmission: on-site and remote

#### Archiving procedures

- Metadata description in the GAW Station Information System (GAWSIS)
- Data should be linked to the World Data Centre for Aerosols (WDCA)

## 8.6 Quality assurance and quality control plans

#### Instruments

- Application of quality test tools at the site
- Intercomparison with reference transportable systems

#### Retrieval algorithms

- Blind intercomparison of raw data processing using synthetic data

#### Comparable datasets

- In order to produce comparable
- Datasets the application of certified data retrieval algorithms should be strictly requested. The development of such retrieval algorithms within GAW is a prerequisite.

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Relevant general and specific information can be found in the presentations made at the Second GALION Workshop available at <http://www.wmo.int/gaw/galion/index.html>.

Further information can also be found at the following lidar networks websites:

- AD-Net - Asian Dust and Aerosol Lidar Observation Network: <http://www-lidar.nies.go.jp/AD-Net/>
- ALINE - Latin America Lidar Network: [www.aline.org](http://www.aline.org)
- EARLINET - European Aerosol Research Lidar Network: [www.earlinet.org](http://www.earlinet.org)
- MPLNET- Micro Pulse Lidar Network: <http://mplnet.gsfc.nasa.gov/>

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## CHAPTER 9. ARCHIVING PROCEDURES

### 9.1 Introduction

The World Data Centre for Aerosols (WDCA) is the data repository and archive for microphysical, optical, and chemical properties of atmospheric aerosol of the World Meteorological Organization's (WMO) Global Atmosphere Watch (GAW) programme. Over the past decade, the demands directed towards a research network data centre, such as a GAW WDC, have changed considerably. When the outgoing GAW Strategic Plan was approved in 2007 (GAW Report No. 172), the objectives for the GAW World Data Centre for Aerosols were induced by the objectives of the GAW aerosol programme:

- ***"...to determine the spatio-temporal distribution of aerosol properties related to climate forcing and air quality at up to multi-decadal time scales"***  
Besides a station network with global coverage observing the aerosol parameters prioritised by the GAW aerosol programme, this objective requires the observed data to be archived with a long-term perspective.
- ***"Since the residence time of aerosol particles is relatively short a large number of measuring stations is needed globally"***.  
WDCA collaborates with regional networks such as the U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE), the UNECE European Monitoring and Evaluation Programme (EMEP), and the EU Aerosols, Clouds, and Trace gases Research InfraStructure Network (ACTRIS) by exchanging data and expertise on quality assurance for increasing the data density and quality.
- ***"The data available from WDCA should be of a known quality and include all information required by a user to permit sensible use of the data"***.  
The data need to be documented with sufficient metadata on operating procedures and observation settings to interpret them even after the responsible principal investigator should become unavailable. This requirement does not contradict the GAW policy to encourage contact between data provider and user to establish new collaborations.

Compared to these objectives that focussed largely on data collection, the new GAW Implementation Plan for 2016 to 2023 adds a number of objectives for WDCs that reflect professionalization of scientific data management and additional demands of the public to scientific networks:

- **Traceability**  
For data, traceability means that all processing steps should be documented in a way to trace the data back to the time of measurement. This is intended to allow for re-processing of the data in case of future improved know-how, even if the responsible investigator is not available. With traceable data, data acquisition, data processing, and quality assurance are separated into a series of small, well-defined steps which are documented and are uniform across a network.
- **Inter-operability**  
International frameworks have set the goal to make data readily discoverable, downloadable, and usable across scientific policy or research networks. Most noteworthy here are Global Earth Observation System of System (GEOSS), the WMO Information System (WIS), the EU INSPIRE directive, and the EU Copernicus programme for earth observation.
- **Operational services, near-real-time data collection and dissemination**  
WIS and Copernicus are working towards making data from research networks available for operation products such as improved weather forecast, air quality prediction, and assessment of model skill. To this end, data need to be collected, auto-processed, and centrally available within 1-3 hours.

Implementing the objectives stated for GAW aerosol, the GAW SAG on Aerosols has defined the a list of aerosol parameters to be observed with priority at participating stations (see Table 1.1).

The extent of the observation programme varies between observatories networked in GAW. The observations are reported by the GAW observatories on a voluntary basis, while the station infrastructure is a contribution of the participating national authorities to the GAW programme.

## 9.2 WDCA architecture

Two sections within the GAW aerosol programme can be distinguished: i) observations by active column remote sensing (lidar); ii) near-surface in situ observations and surface passive remote sensing. The active column remote sensing observations by lidar are organized in the GAW Aerosol Lidar Observation Network (GALION). The GALION observation data are currently collected in the data centres of the participating lidar networks:

- Aerosols, Clouds, and Trace gases Research InfraStructure (ACTRIS) lidar network
- Asian Dust Network (AD-Net)
- American Lidar Network (ALINE)
- Atmosphere aerosol and ozone monitoring in CIS regions through Lidar stations Network (CIS-LiNet)
- Latin American Lidar Network (LALINET or ALINE)
- Micro-Pulse Lidar Network (MPLNET)
- Network for the Detection of Atmospheric Composition Change (NDACC)
- NOAA Cooperative Remote Sensing Science and Technology (CREST) Lidar Network (CLN)
- Regional East Aerosol LIDAR Mesonet (REALM)

The intention has been expressed to connect these networks through a common portal for data discovery and access.

For the near-surface in situ and surface passive remote sensing observations, the WDCA data holdings are hosted in the EBAS database, which was originally designed for the [European Monitoring and Evaluation Programme \(EMEP\)](#). Today, EBAS is a long-term data archive for atmospheric composition data, predominantly from near-surface, in situ observations. WDCA data are identified within EBAS with the framework associations GAW-WDCA for fully quality assured data, and GAW-WDCA\_NRT for near-real-time (NRT) data.

WDCA data collection follows two different modes:

### 1) **Regular data reporting**

Delivery of final, quality assured data (level 2, see below for terminology), usually for a whole year at a time. Deadline for reporting is the end of the year following the year data are collected (i.e. year N reporting by end of year N+1). By becoming a GAW member, stations are making a commitment to report their data in this mode. Traceable data reporting is offered for regular data submissions. Contributing networks are not required to submit data to WDCA but must make their data available through their data centres (see WMO, 2016 for GAW and contributing station requirements).

### 2) **Near-Real-Time (NRT) data reporting**

Delivery of annotated raw data (level 0, see below) in blocks of 1 to max. 3 hours duration, starting and ending at the turn of an hour, delivered right at the end of the reporting time interval. NRT data reporting is offered for a selected set of aerosol variables. Participation in the programme is voluntary, but encouraged.

Data providers benefit from improved data dissemination through WDCA with an increased number of collaborations. Data submitted to WDCA are protected by a [fair-use data policy](#) as follows:

“For scientific purposes, access to GAW WDCA data is unlimited and provided without charge. By their use you accept that an offer of co-authorship will be made through personal contact with the data providers or owners whenever substantial use is made of their data. In all cases, an acknowledgment must be made to the data providers or owners and to the data centre when these data are used within a publication.”

An exception to this data policy are NRT data. Due to their nature of being automatically processed, thus having a larger systematic uncertainty and being more demanding to interpret; and due to their limited validity before being superseded by the regularly reported, manually quality assured version; NRT data are available by special agreement between GAW and the user institution or framework. The following data policy applies to NRT data:

“Data delivery on a near-real-time (NRT) schedule is a WMO-GAW pilot project. Near-real-time aerosol data are raw, automatically processed data that have not passed through any review by aerosol scientists. They are intended for applications where gaps and glitches in the data are expected and accepted, for example, assimilation by air quality forecast models. Near-real-time data should not be used in lieu of final, "clean", regularly reported data, and the data providers expressly deny permission for users to publish near-real-time data. Access to WDCA NRT data requires a registration and the user's consent not to distribute or publish data without agreement of the data provider. In the pilot project phase, requests for registration will be evaluated by the GAW Scientific Advisory Group for aerosol. Contact between data users and providers is strongly encouraged. Data providers are very interested in learning about how the data are being used.”

For both data collection modes, regular and NRT data reporting, the standard data flow goes from the station directly to WDCA hosted in the EBAS database, either via anonymous, blind-drop FTP (regular data reporting) or by FTP with station-specific login (NRT data reporting). WDCA data collection, both for regular and NRT data contributions, may also be assisted by sub- or contributing networks, which collect the data from their participating stations, and deliver them annually as regular, manually quality controlled submissions, or pre-processed as NRT data. These sub- or contributing networks include:

- The GAW Precision Filter Radiometer (PFR) network, administered by the World Optical Depth Research Calibration Centre (WORCC) in Davos, Switzerland. The PFR network delivers both regular and NRT aerosol optical depth data measured by ground-based passive remote sensing from currently 24 stations worldwide.
- The federated aerosol network coordinated by the U.S. National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD). The NOAA ESRL GMD aerosol network delivers both regular and NRT data of near-surface in situ aerosol optical and microphysical properties from currently 23 stations worldwide.
- The near-surface in situ network of the ACTRIS. ACTRIS near-surface in situ delivers both regular and NRT data of near-surface in situ aerosol optical and microphysical properties from currently 29 stations worldwide, but mainly Europe.
- The U.S. Interagency Monitoring of Protected Visual Environments (IMPROVE) network. IMPROVE reports regular, manually quality assured data of near-surface in situ aerosol optical properties from currently 11 U.S. American stations.

### **9.3 Implementation of data traceability**

Data traceability is implemented at WDCA with a system of data levels. The goal is to have a data format template for each supported atmospheric aerosol observable and data level (Table 9.1):



**Table 9.1. Description of data levels used in reporting GAW information**

<i>Data Level</i>	<i>Description</i>		<i>Used For</i>
0	<ul style="list-style-type: none"> <li>• Annotated raw data</li> <li>• Format is instrument specific</li> <li>• Contains all parameters provided by instrument as provided</li> <li>• Contains all parameters / info needed for processing to final value.</li> <li>• "Native" time resolution</li> </ul>		<ul style="list-style-type: none"> <li>• Advanced data reporting</li> <li>• Near-Real-Time (NRT) data reporting</li> </ul>
1	<ul style="list-style-type: none"> <li>• Data processed to final parameter</li> <li>• Invalid data and calibration episodes removed</li> <li>• Extreme and special events marked by appropriate flag.</li> <li>• "Native" time resolution</li> <li>• Format is property specific</li> <li>• Correction to standard temperature and pressure condition (273.15 K, 1013.25 hPa) if necessary</li> </ul>		<ul style="list-style-type: none"> <li>• Advanced data reporting</li> <li>• Intercomparisons</li> </ul>
1.5	<ul style="list-style-type: none"> <li>• Data aggregated to hourly averages</li> </ul>	auto-processed	Near-Real-Time (NRT) data processing
2	<ul style="list-style-type: none"> <li>• Atmospheric variability quantified by standard deviation or percentiles</li> <li>• Format is property specific</li> </ul>	manual quality assurance	Regular, annual data reporting

Standard Operating Procedures (SOPs), such as those mentioned in this report, describe the processing steps between data levels. The SOPs are referred to in the metadata item called "Standard method" in the data file header. A regular, annual data submission consists only of data in level 2 format.

## **9.4 Submitting data to the World Data Centre for Aerosol**

### **9.4.1 Standard, regular data reporting**

#### **Data quality**

For most types of aerosol observations in the GAW network, the SAG Aerosol has made a list of recognised measurement and data handling procedures, including references to the scientific literature. Please also have a look at the remainder of this report and [GAW Report No. 200](#) (SOP for measurements of particle mass concentration, light scattering and absorption). The header of the data files contains a field specifying which of these procedures was used. A list of the procedures available for each parameter is contained in the parameter specific data file templates. Even if a dataset does not yet conform to any of these procedures, it may be submitted to WDCA, but it needs to be stated that none of the mentioned standard operating procedures has been used.

#### **Submission format**

Data submitted to WDCA need to be formatted in the EBAS NASA-Ames format by the data provider. The work of assembling the data into the reporting format is assigned to the data provider for the following reasons:

- 1) **Avoiding of errors:** Reformatting the data for the provider increases the number of errors in the data. The reformatting process often involves lengthy correspondence between data provider and data centre on how to interpret the data, and is prone to

misunderstanding and information loss. A clearly defined format as interface between data provider and centre avoids this information loss.

- 2) **Scientific standard of data provider:** The annual data submission represents the essence of a year's scientific work at the station. It is part of most data providers' standard and their own wish to assemble this part of their work themselves.
- 3) **Work load at data centre:** The EBAS database that is hosting WDCA collects over 6000 datasets per year, including co-operating networks. With reformatting this amount of data, the number and quality of other data centre services would be rather limited. Together with data providers and users, it was decided to free these resources in favour of data interpretation and dissemination.

The data format is based on the ASCII text NASA-Ames 1001 format (ASCII and UTF-8 character sets allowed), but contains additional metadata specifications ensuring proper documentation, and is designed to be easily understandable. Reasons for using this format include:

- 1) **Simplicity:** EBAS NASA-Ames consists of a pure ASCII text that may be assembled and used with numerous, readily available spreadsheet applications, plotting applications, and numerical libraries. It is readable and understandable. It is streamlined enough to make the instructions on assembling it fit on a few pages, which is rarely matched by other formats, but still contains the essential information for efficient data archiving, discovery, and documentation.
- 2) **Reduce format confusion:** Some features and specifications of NASA Ames 1001 and EBAS NASA-Ames are targeted at older IT environments. However, since necessary new features can be implemented within the existing format, defining an only slightly optimised new format would add to the format confusion and prevent the use of existing routines and libraries.
- 3) **Keep threshold low:** Other formats like NetCDF or HDF have come into use in the modelling and satellite communities, respectively. These binary formats are not plainly readable for a human, and special applications or routines as well as a steep learning curve are required for assembling them. For EBAS, it is the intention to keep the threshold for data providers as low as possible. EBAS NASA-Ames has been in use for well more than a decade, and is used also by countries with less developed atmospheric monitoring infrastructures.

The [WDCA webpage](#) contains a "Submit" section with file format templates for submission of data from supported observation types. Both the list and the templates themselves are non-static, but updated continuously to accommodate new observation types and new requirements for improving data documentation. A list of these templates can be found in Annex A.

### Submission procedure

The usual steps for submitting data include:

- 1) **Registering the station with GAWSIS**  
Stations submitting data to WDCA for the first time need to ensure the station is already registered with the GAW Station Information System (GAWSIS, <https://gawsis.meteoswiss.ch>). If not yet registered, either the person responsible for the station as a whole, or another authorised person may register the station. After contacting WDCA by e-mail ([ebas@nilu.no](mailto:ebas@nilu.no)), this person will receive login credentials for GAWSIS. After login, the menu item "Register a new station" is available in GAWSIS, where a form needs to be filled in to complete the station registration.
- 2) **Initial contact with WDCA**  
The data submitter should establish an initial contact with WDCA by writing an e-mail to

[ebas@nilu.no](mailto:ebas@nilu.no). In this mail, the GAW SIS station ID (obtained via registration in GAW SIS) and the parameters to be reported should be indicated. In return, the data submitter will receive three further IDs: i) the EBAS station code; ii) the EBAS platform code; iii) a code for your lab analysing the data, which you will need for the metadata in your submission. The reason for having several station codes lies in several collaborating frameworks. The three letter GAW IDs and the IDs used in the CLRTAP EMEP database EBAS were introduced independently and are maintained for consistency.

### 3) **Data quality assessment**

Quality assessment is the most labour intensive and most important step in data reporting, and a prerequisite for any further use of the data. The standard operating procedure (SOP) for the parameter or instrument type should be applied both during data collection as well as data processing and evaluation. There will likely be periods for which data are invalid due to calibrations or malfunctions, and there may be additional conditions (activity around the station, etc.) necessary to convey to the data user. WDCA uses a system of flags for this purpose. Each flag is assigned a 31 digit integer number. The flags commonly used for a data type are listed on the same page as the corresponding data format template. Additional flags are listed in the complete flag list at <http://www.nilu.no/projects/ccc/flags/flags.html>. The list of flags is comprehensive, but may not be complete. Further flags can be requested by sending an e-mail to [ebas@nilu.no](mailto:ebas@nilu.no).

### 4) **Assembling/updating metadata header:**

#### a. **First-time submission**

In assembling the header with metadata for a first-time data submission, it is reasonable to copy the template for the parameter to be reported from the WDCA webpage, and to adapt it to the station and protocols used for data collection and processing. Each line in the online template, or the respective line number, is a link pointing to an explanation of the content. The explanation always begins with a specification of the syntax used. Items enclosed in "<>" mark a place holder to be replaced with content or key words as described. The syntax should be followed exactly since many lines contain a keyword identifying the content, and these keywords are recognised by string comparison. Either ASCII or UTF-8 character settings should be used.

#### b. **Continuing submission**

For stations and parameters that have been previously reported to WDCA, the header from the previous year can be copied and updated. All metadata items should be checked and updated in case any changes occurred in the instrument setup. Especially for later trend analysis, it is rather important that any changes that may have caused a rupture in the dataset are documented in the metadata.

### 5) **Formatting data, joining header and data sections**

The data section of an EBAS NASA-Ames file consists of a fixed width, fixed number format ASCII table, with the number formats specified in the file header. Once the data section is constructed, header and data section are joined into 1 file having the file name used in the header.

### 6) **Submitting data**

The files containing the data submissions are uploaded to EBAS's anonymous FTP-site, which is accessible at:

<ftp://gaw-wdca.nilu.no/incoming>

To prevent abuse, this server is configured in "blind-drop" mode. It accepts uploads only and ignores directory requests, i.e. uploaded files cannot be seen. It is impossible to delete files once they were uploaded. When uploading a file in error, an e-mail to [ebas@nilu.no](mailto:ebas@nilu.no) should specify the details. An automated acknowledgement of receipt will

be sent to all e-mail addresses stated in the submitted file for principal investigators and data submitters if the data type is recognised and the file name syntax is correct. A page summarising the [submissions status](#) is available as well, even if the data submission is not visible yet in the database, e.g. because of format issues to be resolved.

## Legacy data

For assessing trends in load and properties of atmospheric aerosol, long time series are of vital importance. The WDCA therefore welcomes submissions not only of recently collected data, but also of legacy data. This includes data that may not yet have been collected in compliance with any standard operating procedure recognised today.

### 9.4.2 *Advanced (traceable) regular data reporting*

Advanced data reporting intends to make data traceable to the time of measurement. For participating in the advanced data reporting scheme, data levels level 0 and 1 are included in the annual data submission in addition to the regular level 2 version, and uploaded the same way. The WDCA home page "Submit" section contains a sub-menu "Advanced Data Reporting" where all level 0 and 1 templates that are available at any given time are listed.

### 9.4.3 *Near-real-time data reporting*

The WDCA NRT scheme aims at collecting, processing, and disseminating data of selected aerosol instrument types within 3 hours, while the target turnover time is 1 hour. This future-oriented service is targeted towards validation of weather forecast models that include atmospheric aerosol, as well as forecast products on air quality and health effects. Current users of the service include the [European Centre for Medium-Range Weather Forecast \(ECMWF\)](#) and the [Aerosol Comparisons between Observations and Models \(AeroCom\)](#) initiative.

The WDCA NRT scheme collects, processes, screens, and disseminates data automatically without regular human intervention. It is therefore expected and accepted that NRT data have a higher uncertainty than manually quality assured regularly reported data. Currently, the following instrument types are supported:

- Nephelometer (aerosol light scattering coefficient)
- Filter absorption photometer (aerosol light absorption coefficient)
- Differential/scanning mobility particle sizer (particle number size distribution for particle diameters < 800 nm)
- Sun-tracking filter radiometer (optical depth of atmospheric aerosol column)

NRT data are submitted in level 0 format to WDCA, where they are processed to level 1.5 and published. To participate in the WDCA NRT scheme, the following steps are necessary:

- An automatic routine generating hourly level 0 data files for the targeted instrument is created. These files should have the same time resolution (interval between data lines) as normal level 0 files, but should start and end at the turn of an hour.
- An example of these level 0 files is sent to [ebas@nilu.no](mailto:ebas@nilu.no) for identifying errors, and iterating with the data provider while errors are present.
- WDCA provides a FTP upload account for the station.
- The stations sets up and activates an automatic hourly FTP upload to the account.

Further enquiries, e.g. on how to generate the level 0 files automatically, should be directed to [ebas@nilu.no](mailto:ebas@nilu.no).

## 9.5 Data curation, data dissemination, user interaction

Once a regular, annual data submission is received by WDCA, it enters a queue system for being processed and ultimately inserted into the EBAS database that hosts WDCA. A software tool checks the submitted file for correct syntax and logical consistency of various metadata items among themselves and with the data, e.g. certain matrices such as PM1 require certain types of inlets, the missing value code used in the data section must correspond to the missing value code indicated in the file header for the respective data column. Errors discovered are relayed to the data submitter with a request to update and re-upload the submission. All data versions accrued in this process are archived offline. Finally, the submitted data are inspected manually by graphical display, e.g. to detect outliers that went unnoticed, before the data are inserted into the database and published. If the submission followed the guidelines for advanced, traceable data reporting, data level 0 and 1 are archived offline alongside with the offline version of the level 2 submission. The level 0 and 1 versions are available on e-mail request to [ebas@nilu.no](mailto:ebas@nilu.no).

WDCA supports two main channels for disseminating its data holdings:

### 1) **Web-interface**

The web-interface of the EBAS database hosting WDCA gives access to both regularly submitted, manually quality assessed data (data level 2), and automatically processed NRT data (data level 1.5). Due to the special data policy for NRT data, access to these requires a login (username / password). The web-interface allows searching the data holdings by country, station, instrument type and measured component. From the search result, datasets can be selected, specifying a time period, and either plotted or downloaded. All access events (plot, listing data, download) are logged for providing offline access statistics by selectable criteria.

### 2) **Bulk-access**

Institutions and frameworks having a mutual agreement with the GAW aerosol programme may receive bulk access to the data holdings. Currently implemented bulk access methods include:

- a. Provision of user defined data packages extracted with the data centre's internal management tools, which are more efficient than the web-interface.
- b. Provision of pre-defined, regularly updated data packages accessible by password protected FTP.
- c. Machine-to-machine interface by the Simple Object Access protocol (SOAP) with the Hypertext Transfer Protocol (HTTP) as transport layer.

Institutes and frameworks making use of these access options include:

- The [Meteorological Synthesizing Centre – West \(MSC-West\)](#) of the UNECE European Monitoring and Evaluation Programme (EMEP) (provision of user-defined data packages)
- The Aerosol Comparisons between Observations and Models (AeroCom) initiative (provision of user-defined data packages)
- The European Centre for Medium-Range Weather Forecast (ECMWF) (provision by password-protected FTP)
- The aerosol network of the U.S. National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) (machine-to-machine access via SOAP).

In addition, WDCA assists ad-hoc initiatives of scientists undertaking targeted studies for regional phenomena, trend assessments, etc. by providing data archiving and provision services.

WDCA's main user interaction pathway is informal, and consists of comments and suggestions received by e-mail exchanges with data providers iterating data submissions, or data users

requesting custom extracts of the data holdings. Furthermore, the EBAS database hosting WDCA has its own, formalized [feedback server](#).

## 9.6 WDCA services outlook

WDCA works continuously on improving its services and adapting them to the changing needs in data management and inter-operability arising from building the WMO WIS and the WMO Integrated Global Observing System (WIGOS). In this task, WDCA collaborates with external projects, most prominently and recently with the EU-funded projects European Supersites for Atmospheric Aerosol Research (EUSAAR), ACTRIS, and its successor ACTRIS-2. Features and services on the roadmap for being implemented include:

- **Data submission portal**

In this web-portal, data providers will be able to check their data submissions for correct syntax and consistency before in fact submitting them. The portal will be based on the same software used internally by the data centre for checking data submissions. In this way, the turn-around time for giving data submitters feedback on their submissions will be reduced, and resources freed at the data centre for other services.

- **Connection to WIS/metadata server**

Inter-operability between data centres and to data portals requires data holdings to be searchable and discoverable with a standard-conforming metadata server. WIS-internally, the OAI-PMH metadata server is used as standard. WDCA works on implementing such a server for its database, and is in the process of becoming a WIS Data Collection or Production Centre (DCPC).

- **Standard-conforming machine-to-machine data access**

The second component of inter-operability among data centres and to data portals is access to the data holdings themselves. This machine-to-machine access should conform to established standards. WDCA is working on implementing web-services for its data holdings conforming to the Open Geospatial Consortium (OGC) standards.

- **Automated data quality assessment**

With manual data quality assessment, either by the data provider or at the data centre, outliers or erroneous data may still pass unnoticed. WDCA is working on two types of automated data quality assessment: i) tests for outliers; ii) consistency of measurements done at the same location, i.e. closure tests between aerosol microphysical and optical properties.

## Contact

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## PARAMETER SPECIFIC FILE FORMAT TEMPLATES

The list of aerosol parameters on which WDCA collects data, and consequently provides templates for data reporting, as well as the templates themselves, are non-static. The list of templates is continuously extended to cover new parameters in the focus of the GAW aerosol programme, or new measurement methods becoming operational at monitoring stations. The templates are updated with further metadata items to make the data self-descriptive if needed, or to make the data conform with documentation requirements arising from interoperability.

This section contains a list of the currently available templates for regular, annual data reporting (data level 2) and advanced, traceable data reporting (data levels 0 and 1). These templates are available at <http://www.gaw-wdca.org/SubmitData.aspx>. A [list of all flags](#) for indicating specific sampling conditions or instrument states is available as an online resource as well.

### Level 2 templates (regular, annual data reporting)

- [Aerosol Chemical Speciation \(Aerosol Chemical Speciation Monitor, Aerosol Mass Spectrometer\)](#)
- [Cloud condensation nuclei concentration / size distribution \(Condensation Nucleus Counter \(with DMPS\)\)](#)
- [Aerosol total particle number concentration \(Condensation Particle Counter\)](#)
- [Aerosol particle number size distribution, fine mode \(Differential/Scanning Mobility Particle Sizer\)](#)
- [Aerosol particle number size distribution, coarse mode \(Aerodynamic/Optical Particle Spectrometer\)](#)
- [Aerosol scattering coefficient \(integrating nephelometer\)](#)
- [Aerosol scattering coefficient, dependence on relative humidity \(scattering humidograph\)](#)
- [Aerosol absorption coefficient \(Filter Absorption Photometer\)](#)
- [Radiometric aerosol optical depth](#)
- [Aerosol particle mass concentration \(measured gravimetrically\)](#)
- [Aerosol particle mass concentration \(measured by equivalent online method\)](#)
- [Inorganic particle-phase chemical composition \(analysis of filter sample\)](#)
- [Particle-phase organic/elemental carbon \(OC/EC\) mass concentration \(thermal-optical analysis\)](#)
- [Particle-phase heavy metal mass concentration \(analysis of filter sample\)](#)

### Level 0 templates (annotated raw data, traceable data reporting, near-real-time submission)

- [Cloud condensation nuclei concentration / size distribution \(Condensation Nucleus Counter \(with DMPS\)\)](#)
- [Aerosol total particle number concentration \(Condensation Particle Counter\)](#)
- [Aerosol particle number size distribution, fine mode \(Differential/Scanning Mobility Particle Sizer\)](#)
- [Aerosol scattering coefficient \(integrating nephelometer\)](#)
- [Aerosol scattering coefficient, dependence on relative humidity \(scattering humidograph\)](#)
- [Aerosol absorption coefficient \(Filter Absorption Photometer\)](#)



**Level 1 templates (traceable data reporting)**

- Cloud condensation nuclei concentration / size distribution (Condensation Nucleus Counter (with DMPS))
  - Aerosol total particle number concentration (Condensation Particle Counter)
  - Aerosol particle number size distribution, fine mode (Differential/Scanning Mobility Particle Sizer)
  - Aerosol scattering coefficient (integrating nephelometer)
  - Aerosol absorption coefficient (Filter Absorption Photometer)
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## LIST OF RECENT GLOBAL ATMOSPHERE WATCH REPORTS\*

149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) (WMO TD No. 1147).
150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans (WMO TD No. 1149).
151. Report of the First CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 18-19 March 2003) (WMO TD No. 1181).
152. Current Activities of the Global Atmosphere Watch Programme (as presented at the 14<sup>th</sup> World Meteorological Congress, May 2003). (WMO TD No. 1168).
153. WMO/GAW Aerosol Measurement Procedures: Guidelines and Recommendations. (WMO TD No. 1178).
154. WMO/IMEP-15 Trace Elements in Water Laboratory Intercomparison. (WMO TD No. 1195).
155. 1<sup>st</sup> International Expert Meeting on Sources and Measurements of Natural Radionuclides Applied to Climate and Air Quality Studies (Gif sur Yvette, France, 3-5 June 2003) (WMO TD No. 1201).
156. Addendum for the Period 2005-2007 to the Strategy for the Implementation of the Global Atmosphere Watch Programme (2001-2007), GAW Report No. 142 (WMO TD No. 1209).
157. JOSIE-1998 Performance of EEC Ozone Sondes of SPC-6A and ENSCI-Z Type (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1218).
158. JOSIE-2000 Jülich Ozone Sonde Intercomparison Experiment 2000. The 2000 WMO international intercomparison of operating procedures for ECC-ozone sondes at the environmental simulation facility at Jülich (Prepared by Herman G.J. Smit and Wolfgang Straeter) (WMO TD No. 1225).
159. IGOS-IGACO Report - September 2004 (WMO TD No. 1235), 68 pp, September 2004.
160. Manual for the GAW Precipitation Chemistry Programme (Guidelines, Data Quality Objectives and Standard Operating Procedures) (WMO TD No. 1251), 186 pp, November 2004.
161. 12<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Toronto, Canada, 15-18 September 2003), 274 pp, May 2005.
162. WMO/GAW Experts Workshop on a Global Surface-Based Network for Long Term Observations of Column Aerosol Optical Properties, Davos, Switzerland, 8-10 March 2004 (edited by U. Baltensperger, L. Barrie and C. Wehrli) (WMO TD No. 1287), 153 pp, November 2005.
163. World Meteorological Organization Activities in Support of the Vienna Convention on Protection of the Ozone Layer (WMO No. 974), 4 pp, September 2005.

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\* (A full list is available at <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>)

164. Instruments to Measure Solar Ultraviolet Radiation: Part 2: Broadband Instruments Measuring Erythemally Weighted Solar Irradiance (WMO TD No. 1289), 55 pp, July 2008, electronic version 2006.
165. Report of the CAS Working Group on Environmental Pollution and Atmospheric Chemistry and the GAW 2005 Workshop, 14-18 March 2005, Geneva, Switzerland (WMO TD No. 1302), 189 pp, March 2005.
166. Joint WMO-GAW/ACCENT Workshop on The Global Tropospheric Carbon Monoxide Observations System, Quality Assurance and Applications (EMPA, Dübendorf, Switzerland, 24 – 26 October 2005) (edited by J. Klausen) (WMO TD No. 1335), 36 pp, September 2006.
167. The German Contribution to the WMO Global Atmosphere Watch Programme upon the 225<sup>th</sup> Anniversary of GAW Hohenpeissenberg Observatory (edited by L.A. Barrie, W. Fricke and R. Schleyer) (WMO TD No. 1336), 124 pp, December 2006.
168. 13<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide Concentration and Related Tracers Measurement Techniques (Boulder, Colorado, USA, 19-22 September 2005) (edited by J.B. Miller) (WMO TD No. 1359), 40 pp, December 2006.
169. Chemical Data Assimilation for the Observation of the Earth's Atmosphere – ACCENT/WMO Expert Workshop in support of IGACO (edited by L.A. Barrie, J.P. Burrows, P. Monks and P. Borrell) (WMO TD No. 1360), 196 pp, December 2006.
170. WMO/GAW Expert Workshop on the Quality and Applications of European GAW Measurements (Tutzing, Germany, 2-5 November 2004) (WMO TD No. 1367).
171. A WMO/GAW Expert Workshop on Global Long-Term Measurements of Volatile Organic Compounds (VOCs) (Geneva, Switzerland, 30 January – 1 February 2006) (WMO TD No. 1373), 36 pp, February 2007.
172. WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015 (WMO TD No. 1384), 108 pp, August 2008.
173. Report of the CAS Joint Scientific Steering Committee on Environmental Pollution and Atmospheric Chemistry (Geneva, Switzerland, 11-12 April 2007) (WMO TD No.1410), 33 pp, June 2008.
174. World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide (WMO TD No. 1416), 50 pp, January 2008.
175. The Ninth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Delft, Netherlands, 31-May – 3 June 2005) (WMO TD No. 1419), 69 pp, March 2008.
176. The Tenth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Northwich, United Kingdom, 4-8 June 2007) (WMO TD No. 1420), 61 pp, March 2008.
177. Joint Report of COST Action 728 and GURME – Overview of Existing Integrated (off-line and on-line) Mesoscale Meteorological and Chemical Transport Modelling in Europe (ISBN 978-1-905313-56-3) (WMO TD No. 1427), 106 pp, May 2008.
178. Plan for the implementation of the GAW Aerosol Lidar Observation Network GALION, (Hamburg, Germany, 27 - 29 March 2007) (WMO TD No. 1443), 52 pp, November 2008.

179. Intercomparison of Global UV Index from Multiband Radiometers: Harmonization of Global UVI and Spectral Irradiance (WMO TD No. 1454), 61 pp, March 2009.
180. Towards a Better Knowledge of Umkehr Measurements: A Detailed Study of Data from Thirteen Dobson Intercomparisons (WMO TD No. 1456), 50 pp, December 2008.
181. Joint Report of COST Action 728 and GURME – Overview of Tools and Methods for Meteorological and Air Pollution Mesoscale Model Evaluation and User Training (WMO TD No. 1457), 121 pp, November 2008.
182. IGACO-Ozone and UV Radiation Implementation Plan (WMO TD No. 1465), 49 pp, April 2009.
183. Operations Handbook – Ozone Observations with a Dobson Spectrophotometer (WMO TD No. 1469), 91 pp, March 2009.
184. Technical Report of Global Analysis Method for Major Greenhouse Gases by the World Data Center for Greenhouse Gases (WMO TD No. 1473), 29 pp, June 2009.
185. Guidelines for the Measurement of Methane and Nitrous Oxide and their Quality Assurance (WMO TD No. 1478), 49 pp, September 2009.
186. 14<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Helsinki, Finland, 10-13 September 2007) (WMO TD No. 1487), 31 pp, April 2009.
187. Joint Report of COST Action 728 and GURME – Review of the Capabilities of Meteorological and Chemistry-Transport Models for Describing and Predicting Air Pollution Episodes (ISBN 978-1-905313-77-8) (WMO TD No. 1502), 69 pp, December 2009, electronic version -July 2009.
188. Revision of the World Data Centre for Greenhouse Gases Data Submission and Dissemination Guide (WMO TD No.1507), 55 pp, November 2009.
189. Report of the MACC/GAW Session on the Near-Real-Time Delivery of the GAW Observations of Reactive Gases, Garmisch-Partenkirchen, Germany, 6-8 October 2009, (WMO TD No. 1527), 31 pp. August 2010.
190. Instruments to Measure Solar Ultraviolet Radiation Part 3: Multi-channel filter instruments (lead author: G. Seckmeyer) (WMO TD No. 1537), 55 pp. November 2010.
191. Instruments to Measure Solar Ultraviolet Radiation Part 4: Array Spectroradiometers (lead author: G. Seckmeyer) (WMO TD No. 1538), 43 pp. November 2010.
192. Guidelines for the Measurement of Atmospheric Carbon Monoxide (WMO TD No. 1551), 49 pp, July 2010.
193. Guidelines for Reporting Total Ozone Data in Near Real Time (WMO TD No. 1552), 19 pp, April 2011 (*electronic version only*).
194. 15<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (Jena, Germany, 7-10 September 2009) (WMO TD No. 1553). 330 pp, April 2011.
195. WMO/GAW Expert Workshop on Global Long-term Measurements of Nitrogen Oxides and Recommendations for GAW Nitrogen Oxides Network (Hohenpeissenberg, Germany, 8-9 October 2009) (WMO TD No. 1570), 45 pp, February 2011.

196. Report of the Second Session of the CAS JSC OPAG-EPAC and GAW 2009 Workshop (Geneva, Switzerland, 5-8 May 2009), (WMO TD No. 1577).
197. Addendum for the Period 2012 – 2015 to the WMO Global Atmosphere Watch (GAW) Strategic Plan 2008 – 2015, 57 pp, May 2011.
198. Data Quality Objectives (DQO) for Solar Ultraviolet Radiation Measurements (Part I). Addendum to WMO/GAW Report No. 146 - Quality Assurance in Monitoring Solar Ultraviolet Radiation: State of the Art (*electronic version only*).
199. Second Tropospheric Ozone Workshop. Tropospheric Ozone Changes: observations, state of understanding and model performances (Météo France, Toulouse, France, 11-14 April 2011), 226 pp, September 2011.
200. WMO/GAW Standard Operating Procedures for In-Situ Measurements of Aerosol Mass Concentration, Light Scattering and Light Absorption (Edited by John A. Ogren), 134 pp, October 2011.
201. Quality Assurance and Quality Control for Ozonesonde Measurements in GAW (Prepared by Herman Smit and ASOPOS Panel), 95 pp. October 2014
202. Workshop on Modelling and Observing the Impacts of Dust Transport/Deposition on Marine Productivity (Sliema, Malta, 7-9 March 2011), 50 pp, November 2011.
203. The Atmospheric Input of Chemicals to the Ocean. Rep. Stud. GESAMP No. 84/GAW Report No. 203. 69 pp. (ISSN: 1020-4873).
204. Standard Operating Procedures (SOPs) for Air Sampling in Stainless Steel Canisters for Non-Methane Hydrocarbons Analysis (Prepared by Rainer Steinbrecher and Elisabeth Weiß), 25 pp. September 2012.
205. WMO/IGAC Impacts of Megacities on Air Pollution and Climate, 309 pp. September 2012 (ISBN: 978-0-9882867-0-2).
206. 16<sup>th</sup> WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2011), Wellington, New Zealand, 25-28 October 2011, 67 pp, October 2012.
207. Recommendations for a Composite Surface-Based Aerosol Network, Emmetten, Switzerland, 28-29 April 2009, 66 pp. November 2012.
208. WMO GURME Workshop on Urban Meteorological Observation Design, (Shanghai, China, 11-14 December 2011).
209. Guidelines for Continuous Measurements of Ozone in the Troposphere (Prepared by Ian E. Galbally and Martin G. Schultz), 80 pp, February 2013 (WMO-No. 1110, ISBN: 978-92-63-11110-4).
210. Report of the Third Session of the CAS Joint Scientific Committee of the Open Programme Area Group on Environmental Pollution and Atmospheric Chemistry (JSC OPAG-EPAC), (Geneva, Switzerland, 27-29 April 2011) (*electronic version only*).
211. Rationalizing Nomenclature for UV Doses and Effects on Humans (CIE209:2014/GAW Report No. 211) (ISBN: 978-3-902842-35-0).
212. Standard Operating Procedures (SOPs) for Spectral Instruments Measuring Spectral Solar Ultraviolet Irradiance, 21 pp. June 2014.

213. 17<sup>th</sup> WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), (Beijing, China, 10 - 13 June 2013), 168 pp. July 2014.
214. Report of the GAW 2013 Symposium and the Fourth Session of the CAS JSC OPAG-EPAC, Geneva, Switzerland, 18-20 March 2013, 82 pp, October 2014.
215. Report of the First Session of the CAS Environmental Pollution and Atmospheric Chemistry Scientific Steering Committee (EPAC SSC), (Geneva, Switzerland, 10-12 June 2014), 32 pp. December 2014.
216. Seventh Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E), Lichtklimatisches Observatorium, Arosa, Switzerland, 16-27 July 2012, 106 pp. March 2015.
217. System of Air Quality Forecasting And Research (SAFAR – India), 60 pp. June 2015.
218. Absorption Cross-Sections of Ozone (ACSO), Status Report as of December 2015.
219. Izaña Atmospheric Research Center, Activity Report 2012-2014, 157 pp. June 2015.
220. Report of the Second Session of the CAS Environmental Pollution and Atmospheric Chemistry Scientific Steering Committee (EPAC SSC), Geneva, Switzerland, 18-20 February 2015, 54 pp. June 2015.
221. Report for the First Meeting of the WMO GAW Task Team on Observational Requirements and Satellite Measurements (TT-ObsReq) as regards Atmospheric Composition and Related Physical Parameters, Geneva, Switzerland, 10-13 November 2014, 22 pp. July 2015.
222. Analytical Methods for Atmospheric SF<sub>6</sub> Using GC- $\mu$ ECD, World Calibration Centre for SF<sub>6</sub> Technical Note No. 1., 47 pp. September 2015.
223. Eighth Intercomparison Campaign of the Regional Brewer Calibration Center for Europe (RBCC-E), El Arenosillo Atmospheric Sounding Station, Heulva, Spain, 10-20 June 2013, 79 pp. December 2015.
224. Ninth Intercomparison Campaign of the Regional Brewer Calibration Center for Europe (RBCC-E), Lichtklimatisches Observatorium, Arosa, Switzerland, 24-26 July 2014, 40 pp. December 2015.
225. WMO/UNEP Dobson Data Quality Workshop, Hradec Kralove, Czech Republic, 14-18 February 2011, 32 pp. April 2016.
226. Coupled Chemistry-Meteorology/Climate Modelling (CCMM): status and relevance for numerical weather prediction, atmospheric pollution and climate research, Geneva, Switzerland, 23-25 February 2015, (WMO No. 1172, WCRP Report No. 9/2016), ISBN: 978-92-63-11172-2, 165 pp. May 2016.

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